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NEW POLYISOIMIDES: AN APPROACH TO IN SITU RIGID-ROD POLYIMIDE FORMATION

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Polymer Branch
Nonmetallic Materials Division

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Final Report for Period March 1983 to August 1985

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In situ generation of rigid rod polyimides was investigated by synthesizing a series of soluble (DMAC) benzidine and p-aminobenzene derivative based polyisoimides. The synthesis was carried out by reacting equimolar amounts of new and commercial diamines with pyromellitic dianhydride and then cyclodehydrating the resulting polyamic acids with DCC to give polyisoimides. The newly prepared polymers had I.V.'s ranging from 0.25 to 1.89. Neat and composite films of the polyisoimides were cast from DMAC and isomerized with heating to produce the rigid rod polyimides. The resulting cured films showed no visible signs of phase separation. A study of the isomerization reaction (polyisoimide to polyimide) was conducted by FTIR.

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In Situ Rigid-Rod Polyimide Formation

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 230303, Work unit Directive 23030307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. I. J. Goldfarb as the ML Project Scientist. Co-authors were Capt. S. J. Wallace, Dr. Loon-Seng Tan, and Dr. F. E. Arnold, Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from March 1983 to August 1985.

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INTRODUCTION

Recent success in the application of isoimide chemistry to the processing problems associated with acetylene terminated polyimide oligomers (Reference 1) has prompted investigations into the extension of this synthetic technique to improve processing of high molecular weight polyimides. One such study by Lau (Reference 2) introduced isoimide functional groups into polyimide precursors and found dramatically lower melting points and improved solubility of the resulting polyisoimides. These results appear to warrant additional investigations into the application of isoimide technology to polyimide processing. Work currently centered at the Polymer Branch of the Materials Laboratory involves the development of processable high molecular weight polyisoimides which can be thermally isomerized (without the loss of volatiles) to the respective polyimides.

Most polyimides are soluble in aprotic solvents only at low molecular weights and precipitate before any appreciable molecular weight is achieved. The use of a soluble polyisoimide precursor can provide high molecular weight without precipitation. Once the desired molecular weight has been obtained, the isolated (metastable) polyisoimide is isomerized to the high molecular weight polyimide (see Figure 1).

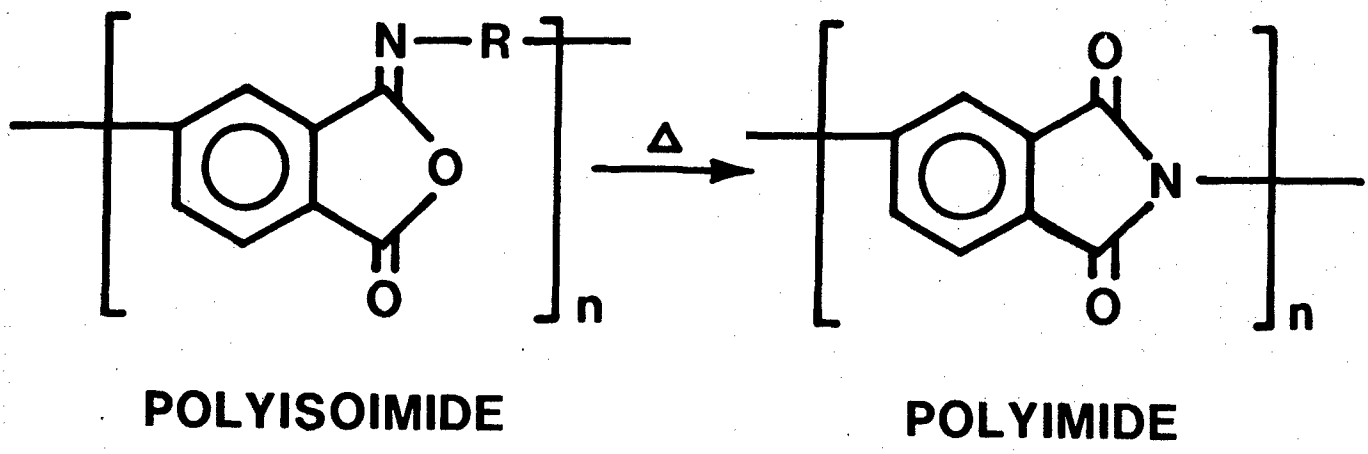
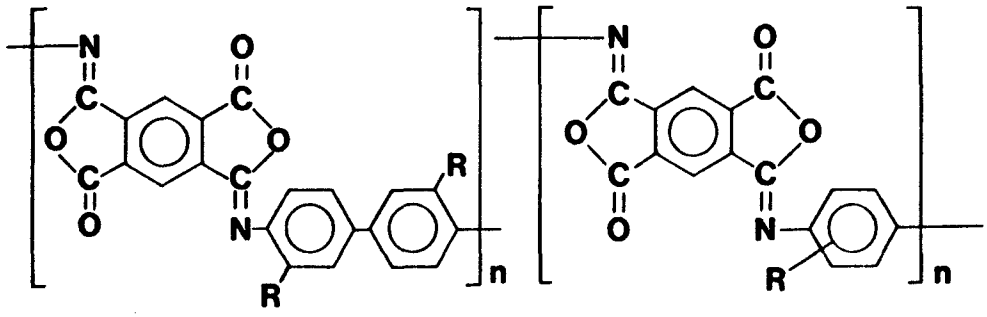


Figure 1. Isoimide to Imide Thermal Isomerization Reaction

Other research has suggested that rod-like polymers of sufficient molecular weight might be good candidates for use in the development of molecular composites (Reference 3). In order to achieve rod-like polyimides, all para structures must be prepared. Work by the Polymer Branch and others has shown that completely para backbone polyimides, and even their polyisoimide precursors, are especially insoluble. An approach to improving the solubility of rod-like polymers has focused on the addition of pendent groups to the rod backbone (References 4 & 5). The increased surface area and interaction with the solvent molecules provided by the pendants should logically improve solubility. With varying degrees of success, both polar and nonpolar functional groups have been employed as pendants (Reference 6).

With these points in mind, it was decided to synthesize a series of high molecular weight polyisoimides with pendent groups which could later be converted to all para polyimide rods. The synthesized isoimides had general structures 1 and 2, where R is a pendent group.

STRUCTURES 1 and 2



1 2

Whenever possible, commercially available monomers were used for synthesis of these systems, but in general, the required diamine monomers had to be prepared in house. Preparation, isolation, and characterization of the polymer systems were carried out using standard techniques (solubility, viscosity, and spectroscopy) and some efforts were made to evaluate the character and extent of the isomerization reaction which occurs when the polyisoimide is converted to the rigid polyimide.

SECTION II

EXPERIMENTAL

1. REAGENTS

The following were purchased from Aldrich Chemical Company and used without additional purification: sodium borohydride (99%), pyromellitic dianhydride (99+%), 3,3'5,5'-tetramethylbenzidine (99+%), 4-nitroaniline, N,N'-dicyclohexylcarbodiimide (DCC) (99%), and isoquinoline (97%). The phenol and 2-phenoxyaniline (which was further purified by sublimation) were purchased from Lancaster Synthesis Ltd. Palladium on carbon (10%) was purchased from K&K Laboratories, Inc., and the 3-phenoxyphenol from Kodak and both were used without further purification. The 3,3'-dichlorobenzidine dihydrochloride was purchased from Sigma Chemical Company and used without further purification. All solvents and inorganic acids and bases were reagent grade. The dimethyl sulfoxide (DMSO) and dimethylacetamide (DMAC) used were further purified by distillation. Silica gel (Noelm Dec) was purchased from ICN Nutritional Biochemicals. Thin layer chromatography (TLC) strips coated with silica gel containing UV-254 indicator were purchased from Brinkman Instruments, Inc.

2. INSTRUMENTATION

Infrared (IR) spectra were recorded with Beckman Model IR-33 and Beckman FT110 spectrometers. Solid sample spectra were obtained from potassium bromide (KBr) films at concentrations of 2% by weight and neat film cast from solution of polymer and DMAC.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian EM-360A spectrometer using 10% weight/volume solutions in deuterochloroform (99.6% gold label) with tetramethylsilane as an internal standard.

Melting points were obtained using a Buchi 510 capillary melting point apparatus.

Elemental analyses were performed by the Analytical Laboratories (AFWAL/MLB), Wright-Patterson Air Force Base, Ohio.

Inherent viscosity measurements were conducted in a constant temperature (30°C) water bath at 1 atm pressure.

3. PREPARATION OF THE AMIC ACID OF 2-PHENOXYANILINE AND PYROMELLITIC DIANHYDRIDE (MODEL COMPOUND)

A 100-ml resin kettle was fitted with a four-necked ground-glass top, mechanical stirrer and nitrogen inlet/outlet. The kettle was charged with 1-phenoxyaniline (1.0000 g, 5.399 mmol), pyromellitic dianhydride (0.5888 g, 2.699 mmol), and 14.29 g of freshly distilled DMAC. After stirring for 2 h, a white precipitate formed in the reaction vessel. The mixture was stirred at room temperature for an additional 12 h. The reaction mixture was filtered. The precipitate was collected, washed with three 100-ml portions of isopropanol, and dried under vacuum at 50°C for 24 h to yield 1.49 g (94%) of a white solid: mp decomposed above 213°C.

Anal. Calcd. for $C_{34}H_{24}N_2O_8$: C, 69.38; H, 4.11; N, 4.76.

Found: C, 69.44; H, 4.61; N, 4.78.

4. PREPARATION OF 2,2'-BENZIDINE ANALOG MONOMERS

3,3'-bis(3-phenoxyphenylene oxy) azobenzene

A three-necked, 250-ml round-bottom flask was equipped with magnetic stir bar, addition funnel and nitrogen inlet/outlet. Under dry nitrogen the flask was charged with sodium borohydride (18.4 g, 0.487 mol) dissolved in 100 ml of dry DMSO. A solution of 3-nitrophenyl(3-phenoxyphenyl)ether (25.0 g, 0.081 mol) in 100 ml of dry DMSO was added to the sodium borohydride solution while stirring over a period of 1/2 h. The addition was accomplished at room temperature and an exotherm noted. The milky-yellow reaction mixture turned red-brown after about 15 min. The reaction was stopped by diluting the mixture with 500 ml of methylene chloride. The methylene chloride solution was washed with three 200-ml portions of 10% hydrochloric acid and one 300-ml portion of distilled water. The bright yellow-orange organic layer was collected, dried (magnesium sulfate), filtered, concentrated (rotary evaporator), and dried under vacuum at 50°C overnight to yield 22.77 g (98.8%) of a dark-orange oil;

Anal. Calcd. for: C, 78.52; H, 4.77; N, 5.09; O, 11.23.

Found: C, 77.91; H, 4.71; N, 5.01; O, 11.79.

2,2'-(3-phenoxyphenylene oxy)benzidine (hydrochloride salt)

To a three-necked, 1000-ml round-bottom flask, equipped with a mechanical stirrer and addition funnel, a solution of stannous chloride (26.85 g, 0.1416 mol) in 250 ml of concentrated hydrochloric acid was added. A solution of 3,3'-bis(3-phenoxy-phenyleneoxy) azobenzene (10 g, 18.16 mmol) in 150 ml of methylene chloride was prepared and added drop-wise over a period of 1 h to the stannous chloride/concentrated hydrochloric acid solution. A light-pink precipitate formed as the addition proceeded. The mixture was stirred overnight and then transferred to a one-neck, 500-ml round-bottom flask and the methylene chloride was removed under reduced pressure with low heat, causing a precipitate (the salt of the newly formed diamine) to form. The precipitate was collected by filtration and washed on a fritted glass funnel with three 100-ml portions of concentrated hydrochloric acid and dried under vacuum at 40°C overnight. The crude salt was stirred with 200 ml of 1N ethanolic potassium hydroxide to produce the free amine. The basic aqueous mixture was extracted with three 100-ml portions of methylene chloride to produce (after drying under vacuum) 9.0 g of a light-brown oil. The oil was chromatographed on a quartz column filled with activated silica gel (600 g). The second band (product) was eluted with n-hexane/ethyl acetate (9/1) to yield 3.11 g (31%) of an off-white viscous oil. The oil was dissolved in 100 ml of a 1:1 mixture of concentrated hydrochloric acid and ethanol. Hydrochloric acid was added until the solution was slightly cloudy, heated until clear, and allowed to slowly cool. A white precipitate formed, was collected, and dried to yield 2.98 g (30%) of while solid: mp decomposed above 120°C; ^{1}H NMR 6.40 - 7.49 (m, aromatic, 24 H), 3.69 (s, amino, 4 H) - for free amine;

Anal. Calcd. for $C_{36}H_{30}O_4N_2Cl_2$: C, 69.12; H, 4.80; N, 4.48; Cl, 11.33.

Found: C, 70.16; H, 5.05; N, 4.93; Cl, 10.60.

5. PREPARATION OF 3,3'-BENZIDINE ANALOG MONOMERS

3,3' DICHLORO-4,4'-DINITROBIPHENYL

STEP 1. Preparation of 3,3'-dichlorobenzidine

150.0 g (0.46 mole) of 3,3'-dichlorobenzidine dihydrochloride was dissolved in 80% ethanol at 50°C under a nitrogen atmosphere. After the solution was at 50°C for 30 min., it was filtered under a nitrogen atmosphere. To the cooled solution 138 g (1.0 mol) of anhydrous potassium carbonate was added in small portions with stirring. After the addition was completed, stirring was continued for an additional 45 min. under nitrogen. The solid which formed was collected by vacuum filtration (N_2) and washed with water, after which the free amine was dried in a vacuum oven at 40° for 48 h. The weight of the free amine obtained from this procedure was 82 g (70% yield).

STEP 2. Preparation of 3,3'-Dichloro-4,4'-Dinitrobiphenyl

To a four-necked, 5 L round-bottom flask, equipped with mechanical stirrer, addition funnel, thermometer, reflux condenser, and ice water bath, were added 1500 ml of methylene chloride and 90 ml of 90% hydrogen peroxide. Once the temperature of the solution was at 10°C, 386 ml of perfluoroacetic anhydride addition was completed. 69.0 g (0.273 mol) of 3,3'-dichlorobenzidine was added in small portions (approx. 5 g each) while maintaining the temperature of the reaction mixture at 10°C. After this, the reaction flask was cooled in an ice bath. The yellow solid which formed was collected by vacuum filtration and washed with water. The filtrate was reduced to one fourth its original volume. The additional solid formed was vacuum filtrated, washed with water, and added to the original precipitate collected. The combined solid was air-dried for 24 h and recrystallized twice from acetone/water (2:1) to yield 61.0 g (0.198 mole; 72.5% yield) of 3,3'-dichloro-4,4'-dinitrobiphenyl which melted at 221-222°C; IR (KBr) 1520, 1325 cm^{-1} (NO_2); 1600, 855, 750 cm^{-1} (aromatic);

Anal. Calcd for $C_6H_6N_2O_4Cl_2$: C, 46.03, H, 1.93; N, 8.95; Cl, 22.65.

Found: C, 45.91; H, 1.96; N, 9.01; Cl, 22.73.

3,3'-(3-PHENOXYO-4,4'-DINITROBIHENYL)

To a 50-ml, three-necked, round-bottom flask, equipped with magnetic stir bar and nitrogen inlet/outlet, was added 30 ml of dry DMSO. While stirring under nitrogen, phenol (3.37 g, 36.0 mmol) and potassium methoxide (2.14 g, 38.0 mmol) were added. The mixture was stirred at 40°C for 1 h after which generation of the potassium salt was judged complete. A 250-ml, three-necked, round-bottom flask was equipped with gas inlet/outlet, addition funnel, and magnetic stir bar and charged with 3,3'-dichloro-4,4'-dinitrobiphenyl (5.0 g, 11.0 mmol) dissolved in 40 ml of dry DMSO (heating to 60°C was required to form a clear-orange solution). The potassium salt of phenol was transferred (under N_2) to the addition funnel and added to the above solution over a period of 1 h. The solution turned much darker and the reaction temperature was maintained at 60°C for an additional 2-1/2 h. The reaction mixture was poured into 700 ml of 1N sodium hydroxide and stirred. A precipitate formed (orange) and was collected by suction filtration, washed (on the filter) with 200 ml of distilled water, dissolved in 200 ml of methylene chloride, dried (magnesium sulfate), and filtered. The filtrate was concentrated (rotary evaporator) and crystallized on standing. The crude orange solid was recrystallized from ethyl acetate/hexanes (1/5) to yield 4.82 g (70.5%) of a light-orange/solid: mp 158-159°C; IR (KBr) 1520, 1325 cm^{-1} (NO_2), 1210 cm^{-1} (ArOAr); ^1H NMR 7.95 - 8.15 (d, aromatic, 2 H), 6.9 - 7.5 (m, aromatic 14H):

Anal. Calcd. for $C_{24}H_{16}N_2O_6$: C, 67.28, H, 3.77; N, 6.54.
Found: C, 67.74; H, 3.89; N, 6.71.

3,3'-(3-PHENOXYPHENYLENEOXY)-4,4'-DINITROBIPHENYL

To a 50-ml, three-necked, round-bottom flask, equipped with magnetic stir bar and nitrogen inlet/outlet, was added 30 ml of dry DMSO. While stirring (under nitrogen) 3-phenoxyphenol (7.45 g, 40.0 mmol) and potassium methoxide (2.95 g, 42.0 mmol) were added. The mixture was stirred at 40°C for 1 h, after which generation of the potassium salt was judged complete. A 250-ml, three-necked, round-bottom flask was equipped with gas inlet/outlet, addition funnel, magnetic stir bar, and charged with 3,3'-dichloro-4,4'-dinitrobiphenyl (5.0 g, 16.0 mmol)dissolved in 40 ml of dry DMSO (heating to 60°C was required to form a clear-orange solution). The potassium salt of 3-phenoxyphenol was transferred (under N_2) to the addition funnel and added to the above solution over a period of 45 min. The solution turned much darker and the reaction temperature was

maintained at 60°C for an additional 2 h. The reaction mixture was poured into 700 ml of 1N sodium hydroxide and stirred. A precipitate formed (orange) and was collected by suction filtration, washed (on a fritted glass funnel) with 200 ml of distilled water, dried (magnesium sulfate), and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (500 g). The second major band (orange) was eluted with methylene chloride/hexanes (4/1) to yield 6.61 g of a yellow-orange crystalline solid which was recrystallized from ethanol/water (5/1) to yield 5.26 g (54%) of light-yellow needles: mp 118.5-119.5°C; IR (KBr) 1510, 1335 cm^{-1} (NO_2), 1230 cm^{-1} (ArOAr); ^1H NMR 7.92 - 8.21 (d, aromatic, 2 H), 6.60 - 7.45 (m, aromatic 22 H);

Anal. Calcd. for $C_{36}H_{24}N_2O_8$: C, 70.57; H, 3.95; N, 4.57.

Found: C, 70.38; H, 4.05; N, 4.79.

3,3'-PHENOXY-BENZIDINE

In a 500-ml Paar hydrogenator flask, equipped with mechanical agitator and high-pressure hydrogen inlet, were added 3,3'-(3-phenoxy)-4,4'-dinitrobiphenyl (3.40 g, 7.94 mmol), 10% palladium on charcoal (0.3 g), magnesium sulfate (2.5 g), and 100 ml of degassed ethyl acetate. The flask was pressurized to 50 psig and agitated 18 h. The resulting clear, colorless solution was pressure-filtered with nitrogen through diatomaceous filter aid which had been previously washed with dry ethyl acetate to remove the catalyst and magnesium sulfate. The clear filtrate was reduced to half the original volume (rotary evaporator) and 75 ml of hexane added. Upon cooling, large off-white crystals formed and were collected by nitrogen pressure filtration to yield 2.72 g of crude crystalline product. The crude crystals were recrystallized from heptane/methylene chloride (10/1) to yield 2.2 g (75.9%) of light-pink plates: mp 126.0 - 126.6; IR (KBr) 3595, 3498, 1622 cm^{-1} (NH_2), 1210 cm^{-1} (ArOAr) (Figure 2); ^1H NMR 6.68 - 7.50 (m, aromatic, 16 H), 3.7 (s, amino 4H);

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60

Found: C, 78.41; H, 5.64; N, 7.69.

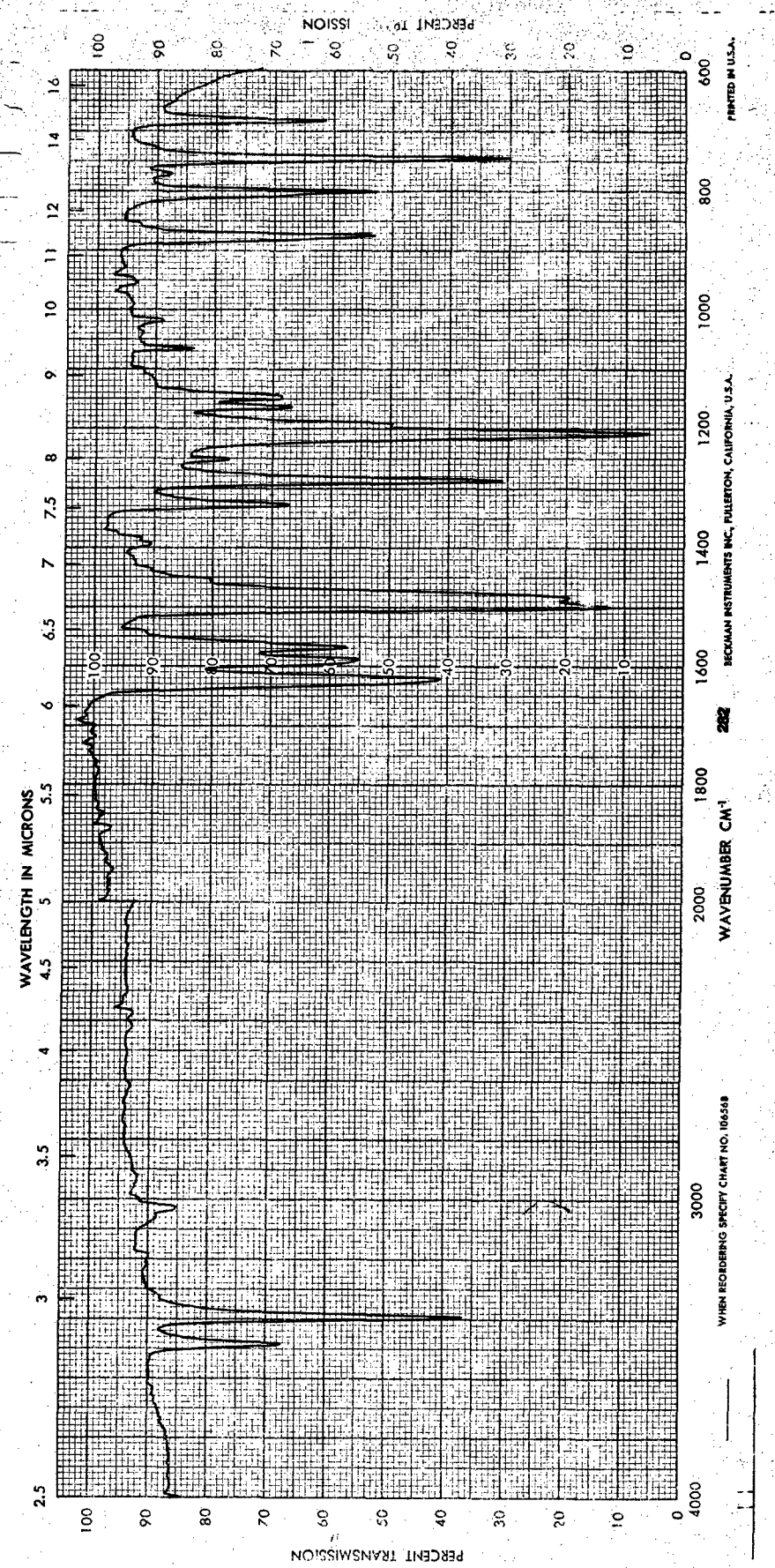


Figure 2. Infrared Spectrum of 3,3'-Phenoxybenzidine

3,3'-(-PHENOXYPHENYLENEOXY)BENZIDINE

In a 500-ml Paar hydrogenator flask, equipped with mechanical agitator and high-pressure hydrogen inlet, were added 3,3'-bis(3-phenoxyphenyleneoxy)-4,4'-dinitrobiphenyl (5.50 g, 9.0 mol), 10% palladium on charcoal (1.0 g), magnesium sulfate (4.0 g), and 150 ml of degassed ethyl acetate. The flask was pressurized to 50 psig and agitated 20 h. The resulting clear off-white solution was pressure filtered with nitrogen through diatomaceous filter aid which had been previously washed with dry ethyl acetate to remove the catalyst and magnesium sulfate. The clear filtrate was reduced by half the original volume (rotary evaporator) and 100 ml of hexane added. Upon cooling, small light-brown crystals formed and were collected by nitrogen pressure filtration to yield 4.79 g of crude crystalline product which was recrystallized from hexanes/toluene (1/1) to yield 3.88 g (78.02%) of off-white crystalline solid: mp 136-137°C; IR (KBr) 3570, 3380, 1628 cm^{-1} (NH_2), 1215 cm^{-1} (ArOAr) (Figure 3); ^1H NMR 6.42 - 7.51 (m, aromatic, 24 H), 3.69 (s, amino, 4 H);

Anal. Calcd. for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 5.11; N, 5.07.

Found: C, 78.25; H, 5.33; N. 5,23.

6. PREPARATION OF 1,4-DIAMINOBENZENE ANALOG MONOMERS

2-BROMO-4-NITROANILINE

100 g (0.724 mol) of p-nitroaniline was slowly added to 1550 ml of glacial acetic acid at 40°C. After cooling the solution to 20°C, 37.4 ml (116.65 g, 0.730 mol) of bromine was added dropwise over a period of one h, after which the solution was allowed to stir an additional 45 min. at 20°C. The precipitate which formed during the reaction was collected by suction filtration and stirred with 2500 ml of 10% aqueous sodium bisulfite for 16 h; collected again by suction filtration and washed with 2500 ml of water. The solid was air-dried for 24 h. The crude material (139 g) was recrystallized twice from 65% methanol to yield 103 g (65.6%) of a yellow crystalline solid which melted at 101-102°C; IR (KBr) 3500, 3400, 1125 cm^{-1} (NH_2); 1500, 1325 (NO_2);

Anal. Calcd. for $C_6H_5N_2O_2Br$: C, 33.18; H, 2.30; N, 12.90; Br, 36.82

Found: C, 33.26; H, 2.28; N, 12.92; Br,

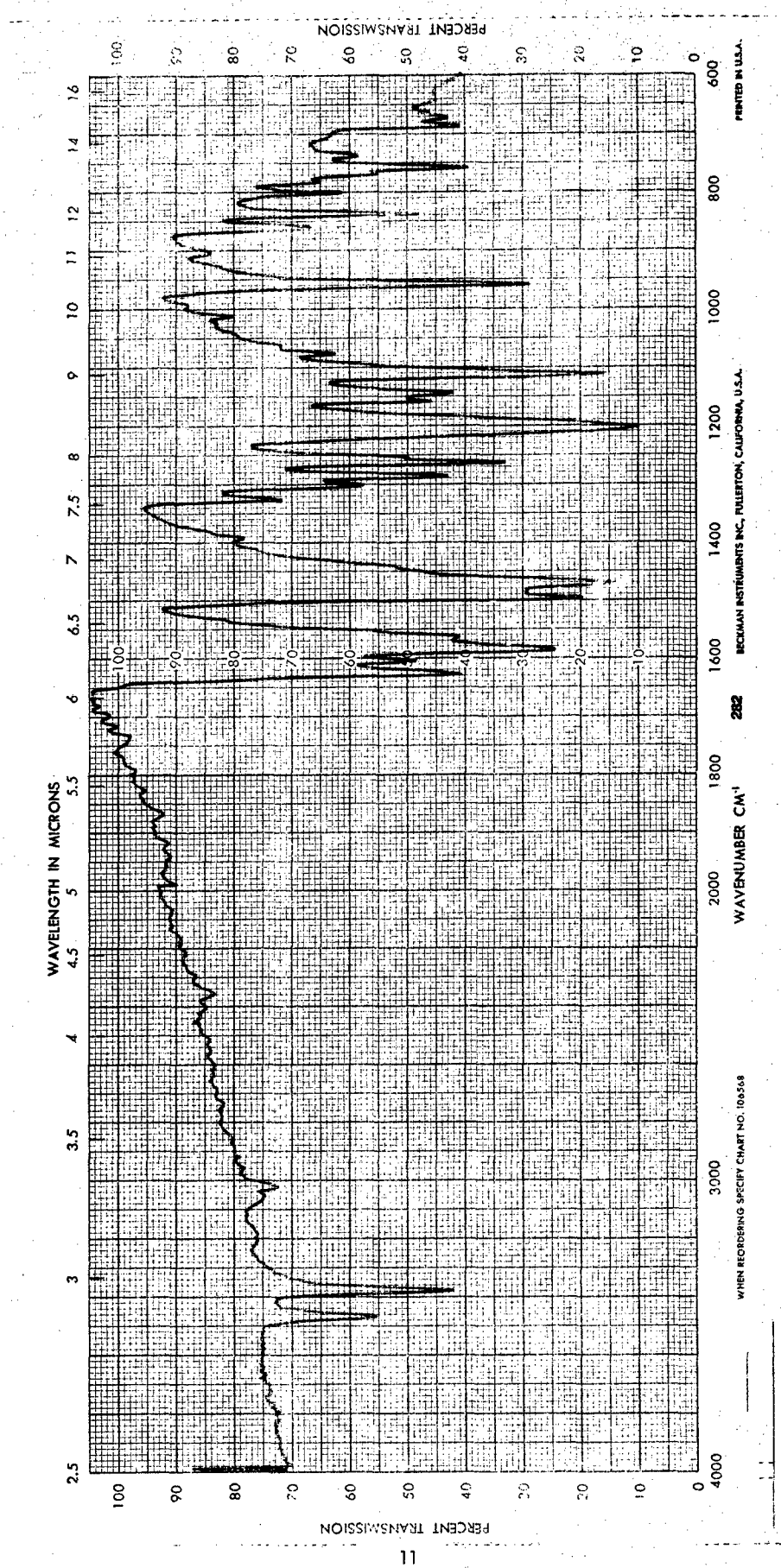


Figure 3. Infrared Spectrum of 3,3'-(3-Phenoxyphenylenedioxy)-benzidine

2-PHENOXY-4-NITROANILINE

A solution of potassium carbonate (9.66 g, 0.07 mol) and phenol (12.99 g, 0.14 mol) was formed with heating (120°) under nitrogen in a three-necked, 50-ml round-bottom flask equipped with reflux condenser, magnetic stir bar, and a gas inlet/outlet adapter. Next, copper-bronze (0.5 g) was added with stirring and the mixture temperature maintained. While stirring, 2-bromo-4-nitroaniline (5.0 g, 0.025 mol) was added in two equal portions and the reaction temperature raised to 135°C and maintained overnight. The dark reaction mixture, while still hot, was poured into 600 ml of 1N aqueous potassium hydroxide and stirred for 1 h. From this procedure a dark-brown precipitate was collected on diatomaceous filter aid by suction filtration. The filter aid and precipitate mixture were extracted with 150 ml of methylene chloride and dried under vacuum. The dark-gray solid (~4.2 g) was chromatographed on a quartz column filled with activated silica gel (400 g). The second band was eluted with methylene chloride/hexanes (1/1) to yield 3.93 g of a yellow-orange solid which was recrystallized from ethanol/water (4/1) to yield 3.61 g (68.1%) of a light-yellow crystalline solid: mp 116-117°C; IR (KBr) 3500, 3360 cm^{-1} (NH_2), 1490, 1290 cm^{-1} (NO_2), 1225 cm^{-1} (ArOAr); ^1H NMR 6.71 - 8.15 (m, aromatic, 8 H), 4.75 (s, amino, 2 H);

Anal. Calcd, for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17.

Found: C, 62.64; H, 4.38; N, 11.78.

2-(3-phenoxyphenyleneoxy)-4-nitroaniline

A solution of potassium carbonate (7.74 g, 0.06 mol) and 3-phenoxyphenol (20.86 g, 0.112 mol) was formed with heating (110°C) under nitrogen in a three-necked, 50-ml round-bottom flask equipped with reflux condenser, magnetic stir bar and a gas inlet/outlet adapter. Copper-bronze (0.5 g) was added with stirring. After mixing well, 2-bromo-4-nitroaniline (6.0 g 0.028 mol) was added in two equal portions and the reaction temperature raised to 135°C and maintained for 5 h. The dark reaction mixture, while still hot, was poured into 700 ml of 1N aqueous potassium hydroxide and stirred for 1 h. From this mixture a fine, dark-brown precipitate was collected on diatomaceous filter aid by suction filtration. The filter aid and precipitate mixture were extracted with 200 ml of methylene chloride, dried (magnesium sulfate), concentrated (rotary evaporator), and dried under vacuum. The dark, red-brown solid (~7.33 g) was chromatographed on a quartz column filled with activated silica gel (500 g). The first major band

(orange) was eluted with methylene chloride/hexane (2/1) to yield 6.9 (6.11)g of an orange-yellow crystalline solid which was recrystallized from isopropanol/water (4/1) to yield 6.61 g (73.2%) of bright-yellow plate-like crystals: mp 121-122°C; IR (KBr) 3500, 3380 cm^{-1} (NH_2), 1500, 1295 cm^{-1} (NO_2), 1210 cm^{-1} (ArOAr); ^1H NMR 7.80 - 8.15 (m, aromatic, 2H), 6.60 - 7.55 (m, aromatic, 10 H), 4.65 (s, amino, 2H);

Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 67.07, H, 4.37; N, 8.69.

Found: C, 67.10, H, 4.49; N, 8.91.

2-phenoxy-1,4-diaminobenzene dihydrochloride

In a 500-ml Paar hydrogenator flask, equipped with mechanical agitator and high-pressure hydrogen inlet, were added 2-phenoxy-4-nitroaniline (3.5 g, 15.2 mmol), 10% palladium on charcoal (0.3 g), and 75 ml of ethanol which had been previously saturated with hydrogen chloride gas. The flask was pressurized to 50 psig and agitated 16 h. The resulting clear, colorless solution was pressure-filtered with nitrogen through diatomaceous filter aid which had been previously washed with hydrogen chloride saturated ethanol to remove the catalyst. The collected filtrate was saturated with hydrogen chloride gas and 50 ml of anhydrous diethyl ether added (causing a slight cloudiness). Upon cooling overnight (0°C) a white precipitate formed, was collected by nitrogen pressure filtration, and dried under vacuum at 60°C over phosphorus pentoxide for 48 h to yield 3.56 g (85.78%) of a white solid: mp decomposed above 120°C; IR (KBr) 1620 cm^{-1} (NH_2), 1205 cm^{-1} (ArOAr) (Figure 4);

Anal. Calcd. for $C_{12}H_{14}N_2Cl_2O$: C, 52.76; H, 5.17; N, 10.26; Cl, 25.96.

Found: C, 49.55; H, 4.71; N, 9.35; Cl, 29.12.

2-(3-phenoxyphenyleneoxy)-1,4-diaminobenzene dihydrochloride

In a 500-ml Paar hydrogenator flask, equipped with mechanical agitator and high-pressure hydrogen inlet, were added 2-(3-phenoxyphenyleneoxy)-4-nitroaniline (4.00 g, 12.4 mol), 10% palladium on charcoal (0.4 g), and 150 ml of ethanol which had been previously saturated with hydrogen chloride gas. The flask was pressurized to 50 psig and agitated 18 h. The resulting clear, colorless solution was pressure-filtered with nitrogen through diatomaceous filter aid, which had

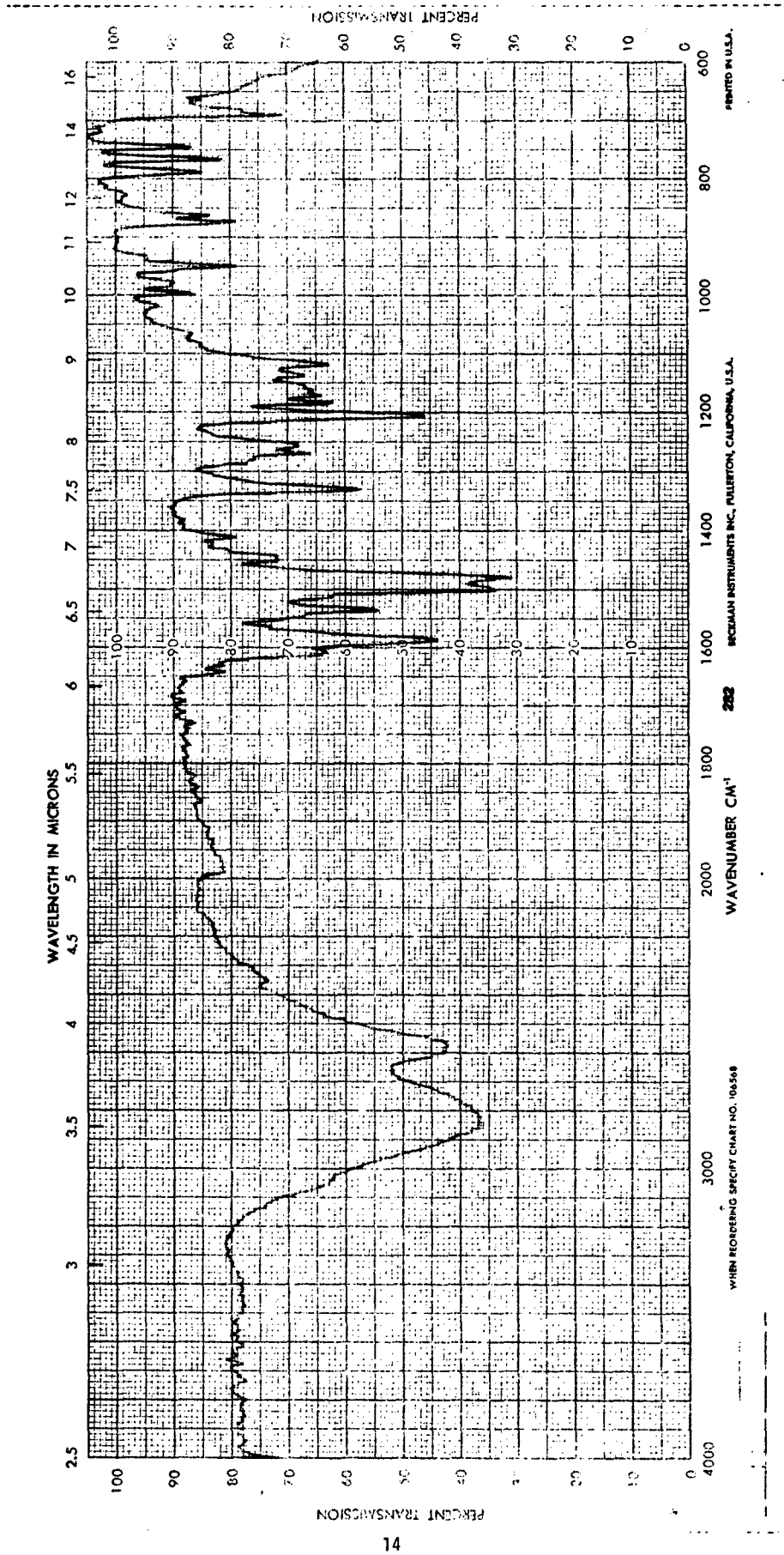


Figure 4. Infrared Spectrum of 2-Phenoxy-1,4-diamino-benzene dihydrochloride

been previously washed with hydrogen chloride saturated ethanol to remove the catalyst. The collected filtrate was saturated with hydrogen chloride gas and 100 ml of anhydrous diethyl ether added (causing a slight cloudiness). Upon cooling overnight (0°C) a white precipitate formed and was collected by nitrogen pressure filtration and dried under vacuum at 60°C over phosphorous pentoxide for 24 h to yield 3.67 g, (81%) of a white solid: mp decomposed above 140°C; IR (KBr) 1627 cm^{-1}) (NH_2), 1215 cm^{-1} (ArOAr) (Figure 5);

Anal. Calcd. for $C_{18}H_{18}N_2O_2Cl_2$: C, 59.19; H, 4.97; N, 7.17; Cl, 19.41.

Found: C, 54.73; H, 4.50; N, 7.15; Cl, 24.16.

7. POLYMER PREPARATION

GENERAL PROCEDURE FOR PREPARATION OF BENZIDINE ANALOG BASED POLYISOIMIDES

A 500-ml, three-necked, round-bottom flask was fitted with a mechanical stirrer and nitrogen inlet/outlet. The flask was charged (under nitrogen) with tetramethyl benzidine (3.04219 g, 12.657 mmol), pyromellitic dianhydride (2.7604 g, 12.6570 mmol) and 58.02 g of freshly distilled DMAC. After stirring at room temperature for 2 h, all of the starting materials dissolved and a significant increase in the reaction mixture viscosity was noted. The reaction mixture was stirred (at room temperature) for an additional 12 h, diluted with 246.95 g of anhydrous DMAC and 1.45 g of anhydrous lithium chloride. The mixture was stirred for 1 h, after which all lithium chloride had dissolved. To this solution, DCC (4.933 g, 23.91 mmol) was added with stirring causing a rapid color change (dark red). The reaction mixture was stirred at room temperature for 12 h, poured into 2400 ml of fresh isopropanol, and stirred for 2 h. A bright red-orange precipitate was collected on a coarse fritted funnel (keeping the material covered with alcohol), washed with three 200-ml portions of fresh isopropanol (again not allowing the material to dry), and finally washed with three 200-ml portions of anhydrous benzene. The final slurry of benzene and product was freeze dried at 0.1-mm Hg for 72 h. This procedure yielded 5.82 g (100.3%) of a bright red-orange fibrous solid.

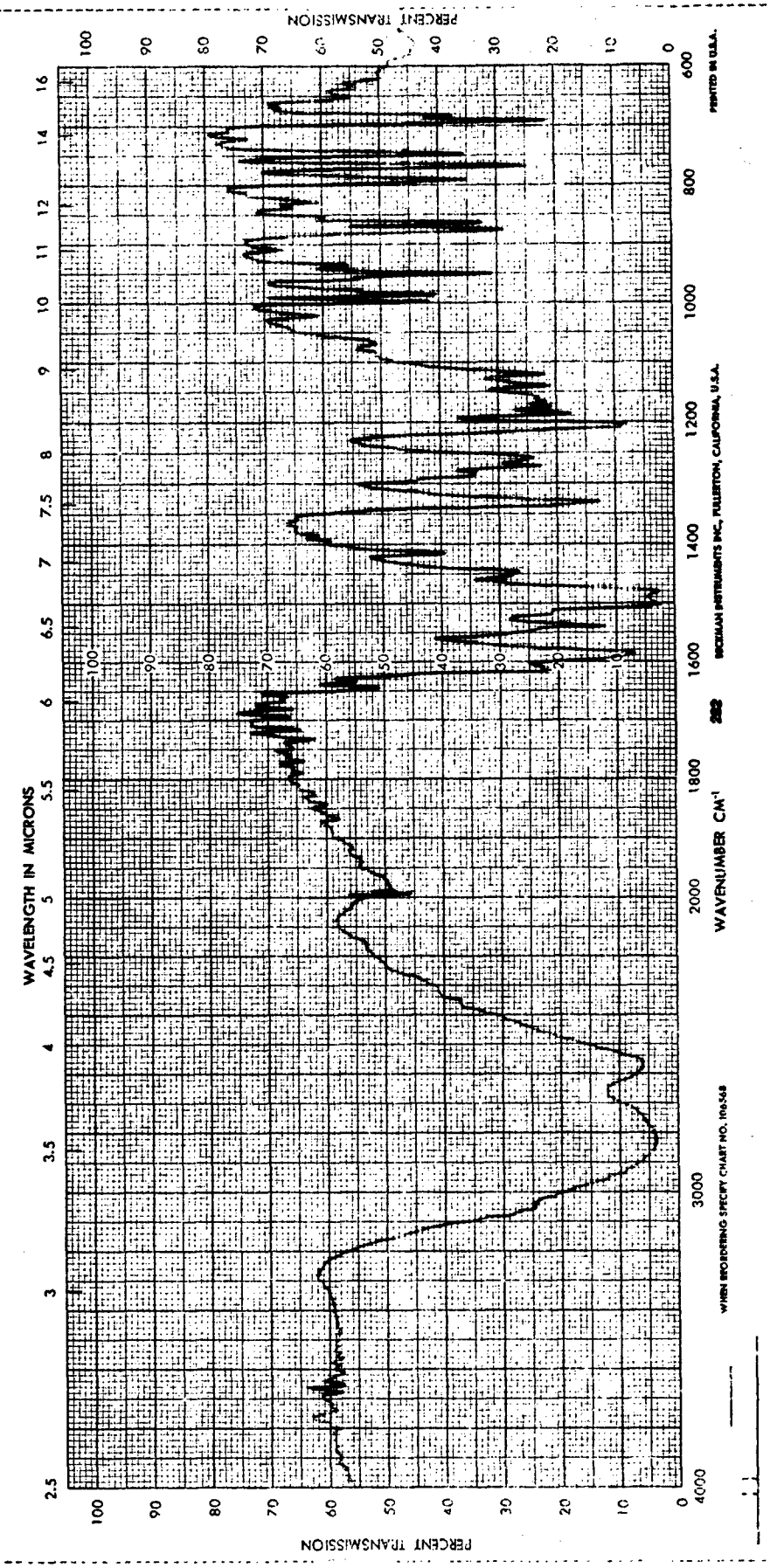


Figure 5. Infrared Spectrum of 2-(3-Phenoxyphenyleneoxy)-1,4-diaminobenzene dihydrochloride

GENERAL PROCEDURE FOR PREPARATION OF 1,4-DIAMINOBENZENE ANALOG BASED POLYISOIMIDES

A 100-ml resin kettle was fitted with a four-necked ground-glass top, mechanical stirrer, and nitrogen inlet/outlet. The kettle was charged with 2-(3-phenoxyphenyleneoxy)-1,4-diaminobenzene dihydrochloride (0.6252 g, 1.712 mmol), pyromellitic dianhydride (0.3734 g, 1.712 mmol), lithium carbonate (0.1130 g, 1.883 mmol) and 9.02 g of freshly distilled DMAC. After stirring at room temperature for a few minutes, evolution of gas was noted and continued for 1/2 h. The light-yellow reaction mixture was stirred (at room temperature) for 12 h, diluted with 43.50 g of anhydrous DMAC, and stirred for an additional hour. To the solution, DCC (0.7205 g, 3.492 mmol) was added with stirring, causing a rapid color change (dark red). The reaction mixture was stirred at room temperature for 12 h, poured into 500 ml of fresh isopropanol and stirred for 2 h. A bright red-orange precipitate was collected on a medium fritted glass funnel, dried briefly under vacuum, redissolved in 50 ml of THF, and reprecipitated in 500 ml of isopropanol. The collected (suction filtration) red-orange solid weighed 0.86 g (98%) after drying at 40°C for 48 h.

GENERAL PROCEDURE FOR PREPARATION OF BENZIDINE ANALOG BASED POLYIMIDES

In a dry 50-ml, three-necked flask, equipped with a magnetic stirring bar, nitrogen inlet/outlet, a short-path distillation apparatus, and a stopper, was placed 2,2'-phenoxybenzidine (1.0110 g, 2.740 mol), pyromellitic dianhydride (0.5985 g, 2.740 mmol), 24 ml of freshly distilled m-cresol, and six drops of isoquinoline. After the diamine dissolved, 15 ml of toluene were added and the reaction mixture slowly heated to 80°C, during which time all the solids dissolved. The reaction mixture was raised to 140°C, at which time the toluene began to distill and a light-yellow precipitate started appearing. After 10 ml of toluene had been distilled, 10 additional milliliters of toluene were added and the temperature raised to 165°C for 2 h, during which time the reaction mixture became filled with light-yellow precipitate (stirring was difficult). The reaction mixture was cooled, the precipitate collected (suction filtration) and washed with three 100-ml portions of methanol. The beige solid weighed 1.27 g (82%) after drying under vacuum at 150°C for 48 h.

SECTION III

RESULTS AND DISCUSSION

1. RESEARCH APPROACH

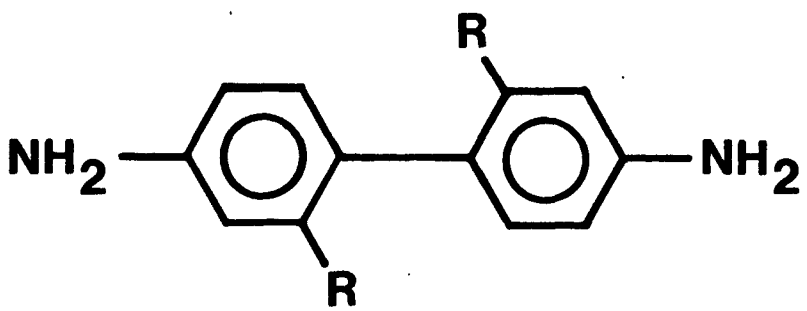
In attacking the solubility problems associated with high molecular weight polyisoimide structures, research was focused primarily on the synthesis and/or purchase of diamine monomers with various types of pendent groups. An alternative approach also being investigated involves the synthesis of dianhydride monomers with pendants (Reference 7). An exhaustive attempt to improve solubility would combine these two approaches. This, as yet, has not been attempted. The synthetic approach for this project involved establishing reaction conditions by adjusting previously established routes to obtain the desired products.

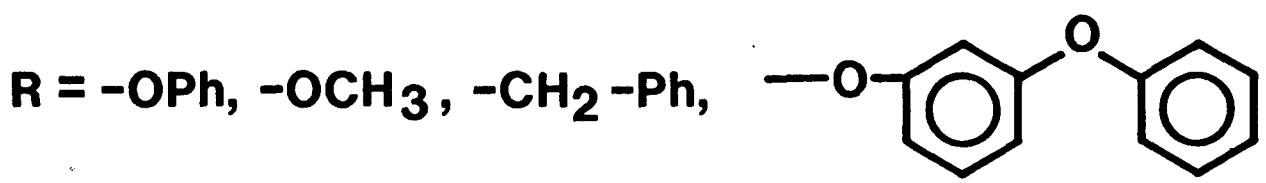
2. DIAMINE MONOMERS

a. 2,2' Benzidine Derivative Synthesis

The first monomer targeted for scale-up and polymerization had the general structure 3 shown below.

STRUCTURE 3





This structure was chosen for its para diamine substitution and the 2,2' substitution of pendent groups which would provide minimal steric hindrance upon polymerization.

The synthesis of the monomers was accomplished by the scheme outlined in Figure 6. Small amounts of all these compounds were tested for solubility in various solvents and monomers with R equal to phenoxy and phenoxyphenyl were found to be the most soluble, with the latter being considerably more soluble than the former.

An attempt was next made to improve the synthesis of the target diamine monomer. An improvement in the synthesis of the monomer was made by substituting sodium borohydride in DMSO for the substituted nitrobenzene reductive coupling reaction (step one). The use of these reagents greatly increased product yield (from 56% to over 95%) and reduced reaction times from ~2.5 hours to one-half hour. The reaction workup was also greatly simplified (see Experimental Section). The second step (a benzidine rearrangement reaction) proved to be a problem. It produced the desired product in only low yield (~30%) along with hard-to-remove side products. High Performance Liquid Chromatography (HPLC) studies showed at least six other products present in the reaction mixture (all in significant amounts). One of the major components, which could be removed fairly easily, was identified as 3-phenoxy phenoxy aniline and was present in about 35%. This seems to indicate that the reduction reaction conditions were too vigorous. The remaining impurities are believed to be isomers of the desired product. The impurities proved to be extremely difficult to remove. Using multiple-column chromatography on silica, fairly pure material was obtained (~98.5% by HPLC), but all attempts to polymerize the monomer failed. Various methods (running the reaction at low temperature, changing reaction solvents, reducing reaction time, etc.) to reduce the amount of side product formation were investigated but no effective procedures were found. A possible reason for the monomers' failure to polymerize is that a hard to detect isomer might still be present even after chromatography. Depending on the isomer's structure it could be considerably less reactive. Attempts at derivatizing and then recrystallizing the monomer also failed to produce polymer-grade monomer.

After the difficulties encountered in the purification of the 2,2' target monomers, it was decided to test the possibility of polymerizing a 3,3' benzidine

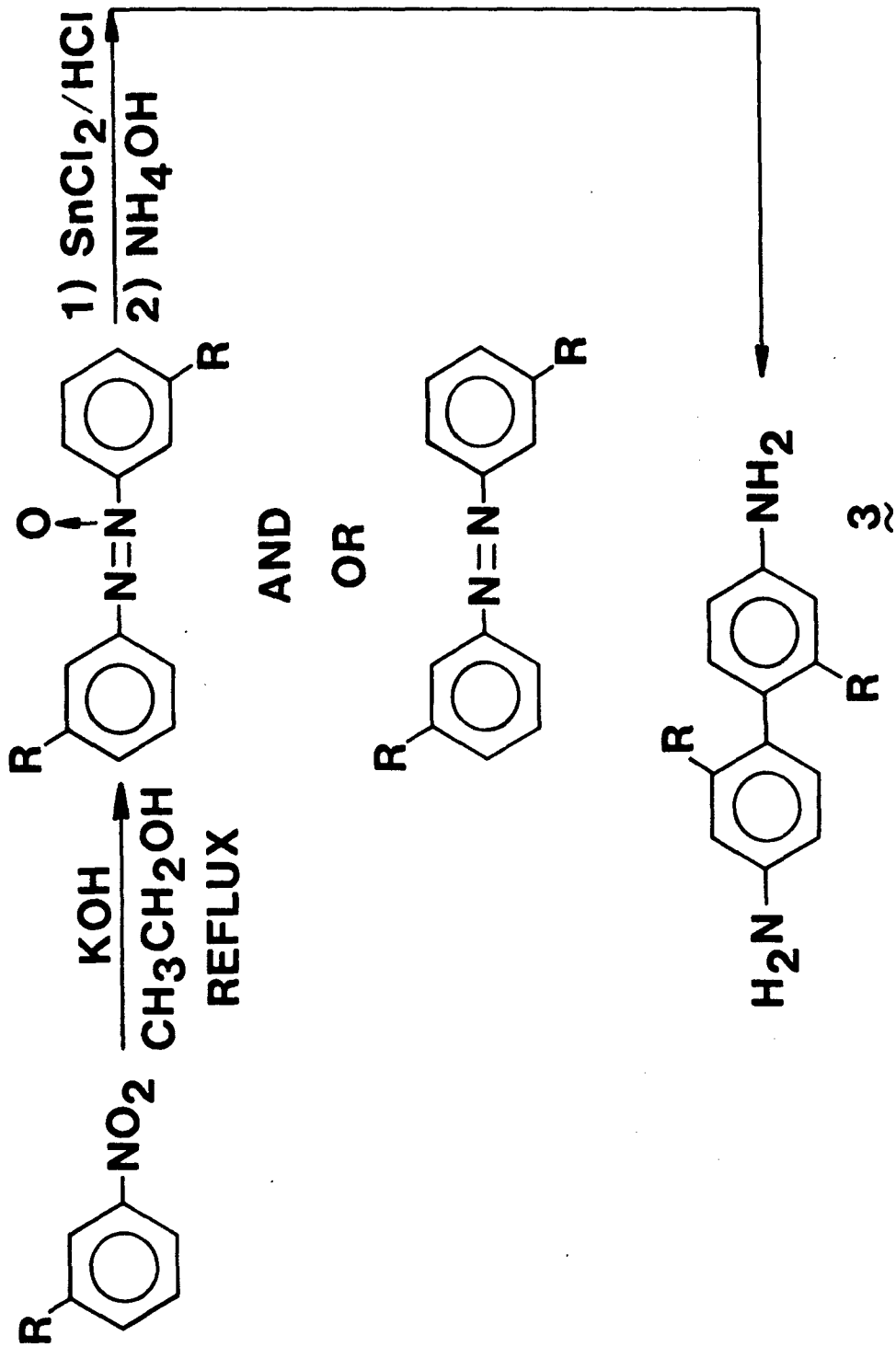
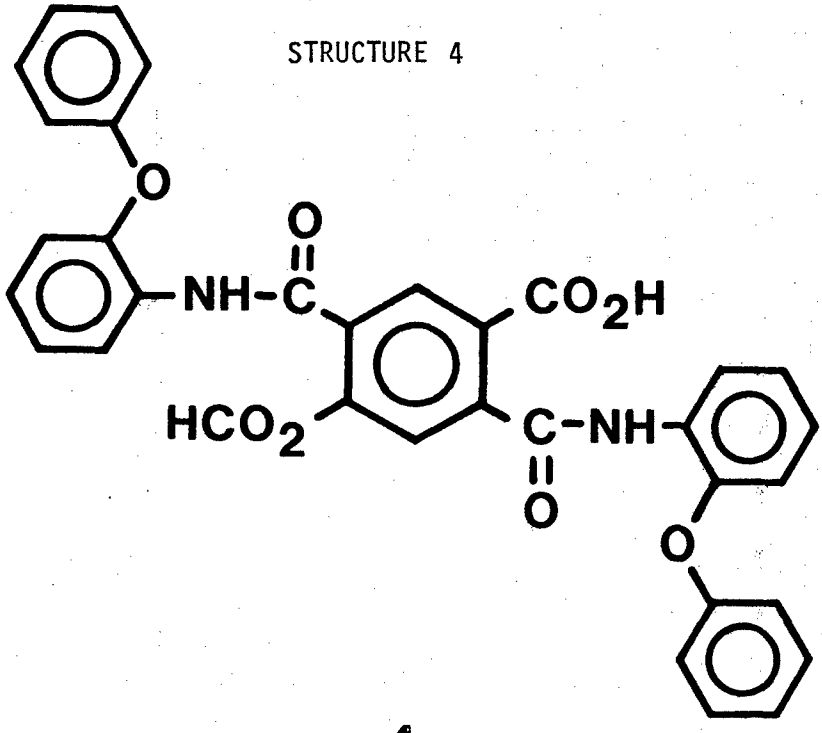


Figure 6. Synthetic Route to 2,2'-Substituted Benzidine Monomers

derivative. It was suggested, with good cause, that a pendent group located in the three position (ortho to the amine functional group) would cause considerable steric hindrance and prevent polymerization from occurring. To investigate this possibility, a model compound with structure 4 was synthesized using identical conditions to a standard diamine-dianhydride condensation polymerization (see Experimental Section).

STRUCTURE 4



4

Evidence (HPLC and Proton NMR) indicated that 4 was produced in a quantitative yield with both the cis and trans (shown above) isomers present.

b. 3,3'-Benzidine Derivative Synthesis

Synthesis of an ortho substituted amic acid model provided a basis for pressing ahead with the development of 3,3'-benzidine derivatives using a synthetic route which avoids any rearrangement reactions. The general approach used to synthesize these derivatives (general structure 5) consists of three basic steps: (1) oxidation of a 3,3' halo-Substituted benzidine compound to a para dinitro biphenyl intermediate, (2) displacement of the halogen groups with pendent substituents, and (3) catalytically reducing the substituted dinitro biphenyl compound to the final pendent substituted diamine. The procedure is outlined in Figure 7.

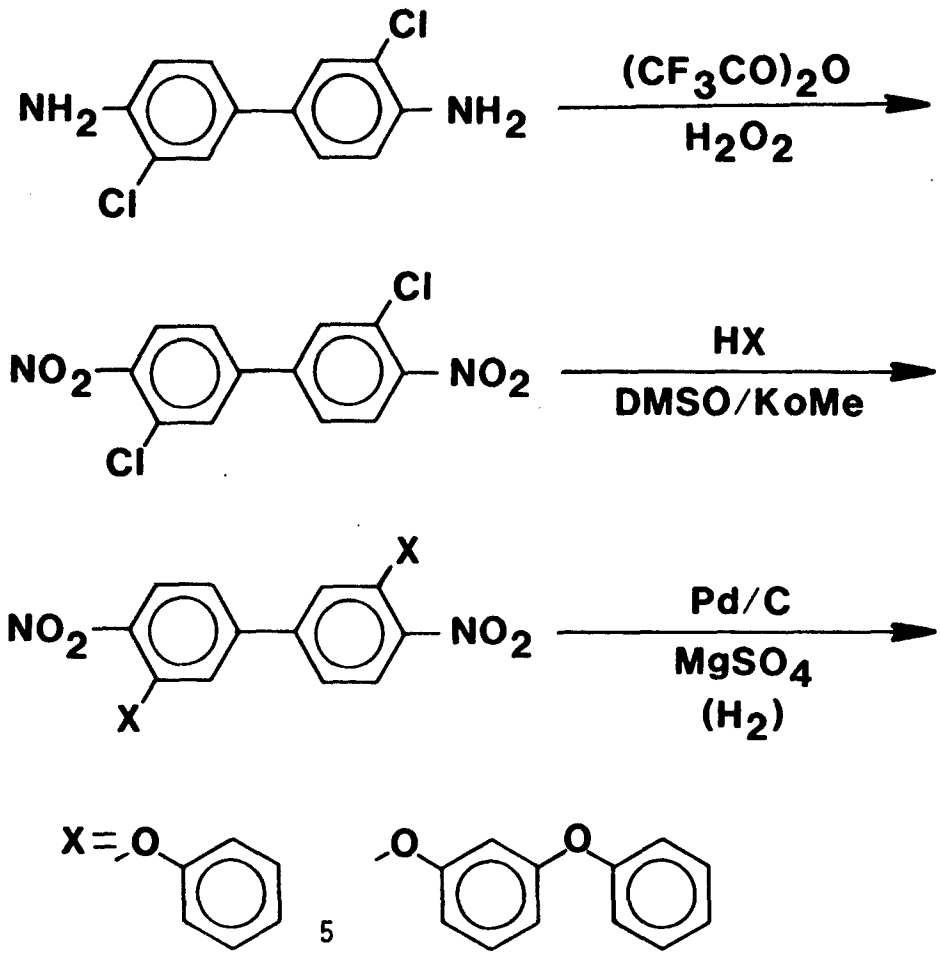


Figure 7. Synthetic Route to 3,3'-Substituted Benzidine Monomers

Oxidation of the 3,3' dichlorobenzidine starting material (purchased from Sigma as the hydrochloride salt) to the dichlorodinitro intermediate was smoothly accomplished using a mixture of perfluoro acetic anhydride and 90% hydrogen peroxide. All reactions were run in methylene chloride, refluxed overnight (~20 hours), and followed by TLC. This synthetic reaction was adapted from a standard procedure (Reference 8). Scale-up of the reaction proved to be easy and gave good yields (~70%).

Reaction conditions developed for the substitution of the pendants was based on nucleophilic substitution of an activated halide. At first an excess of the desired phenolic pendant was used to assure complete substitution, but because of the highly activated chloro leaving groups (ortho to a nitro group) it was determined that only a stoichiometric equivalent was required to complete chloro displacement. The general procedure involves: (1) the generation of a potassium salt (by reaction with potassium methoxide) of the phenolic pendant in DMSO, (2) addition (under nitrogen atmosphere) of the salt to a solution of the dichlorodinitro-biphenyl intermediate, and (3) the maintenance of reaction conditions until product formation is judged complete by the TLC analysis.

Displacement of the chloro leaving groups proceeded very quickly with good yields (60-70%) at 60°C. Reaction rate appeared to be somewhat fast at 60°C (some side product formation was noted by TLC) but a temperature of 60°C was required to dissolve the starting material, dichlorodinitrobiphenyl, in the DMSO solvent. Use of other solvents was not investigated.

c. Another 3,3'-Benzidine Derivative (3,3'5,5'-tetramethyl benzidine)

In an effort to evaluate the solubility of an alkyl group pendant derivative of benzidine, a search of commercially available, polymer-grade monomer was conducted. As a result of the review, an interesting candidate was found. The compound was 3,3', 5,5'-tetramethylbenzidine (99+%) manufactured by Aldrich Chemical Company. This monomer was of interest for two reasons. First, it provided a test case to see if an even more hindered (diortho substitution to the amine) benzidine analog could be polymerized and second, if so, what effect would four pendent groups have on the solubility of the resulting polymer. Some reason

for success was warranted because the pendants were activating alkyl groups and relatively small in size. Polymerization of the monomer was indeed successful and polymers with good inherent viscosities were produced. (See Polymer Synthesis in Results and Discussion Section.)

d. 1,4-Diaminobenzene Derivative Synthesis

In addition to the benzidine analog monomers synthesized, it was of interest to see if single ring diamine monomers would provide soluble isoimide polymers. The procedure developed for the synthesis of these compounds is quite similar to that of the benzidine derivatives. In the first step para nitroaniline is brominated with bromine in acetic acid (the ring is well activated by the amine group) to produce 2-bromo-4-nitroaniline. The procedure works well, but, as expected, some dibromo product is formed. This impurity was removed by recrystallization. The reaction was easy to scale-up and gave yields of 60-70%. The next step used an Ullman ether coupling reaction. The brominated nitroaniline compound was reacted with an excess of the phenolic pendant and a copper-bronze catalyst. The base used was potassium carbonate. As with most Ullman coupling reactions, yields were moderate (50-60%) and side product formation was noted by TLC. In the final step, the pendent-substituted nitroaniline was catalytically reduced, followed by in situ generation of the hydrochloride salt of the diamine. Yields for this step were only fair as compared to most catalytic reductions (60-70%). The synthesis scheme is outlined in Figure 8. The hydrochloric salts of the diamine monomers were fairly stable, but all attempts (as might be expected because of the electron donating phenoxy group) to isolate the free amines in high purity failed. The free diamines were found to be extremely susceptible to oxidative degradation.

3. POLYMER SYNTHETIC

a. Preparation of Benzidine Derivative Polyisoimides

The general approach to the synthesis of the benzidine derivative polyisoimides (three of which were synthesized) involves two synthetic steps: (1) synthesis of a polyamic acid from starting diamine/dianhydride monomers and (2) cyclodehydration of the polyamic acid with N,N'-dicyclohexylcarbodiimide (DCC) to

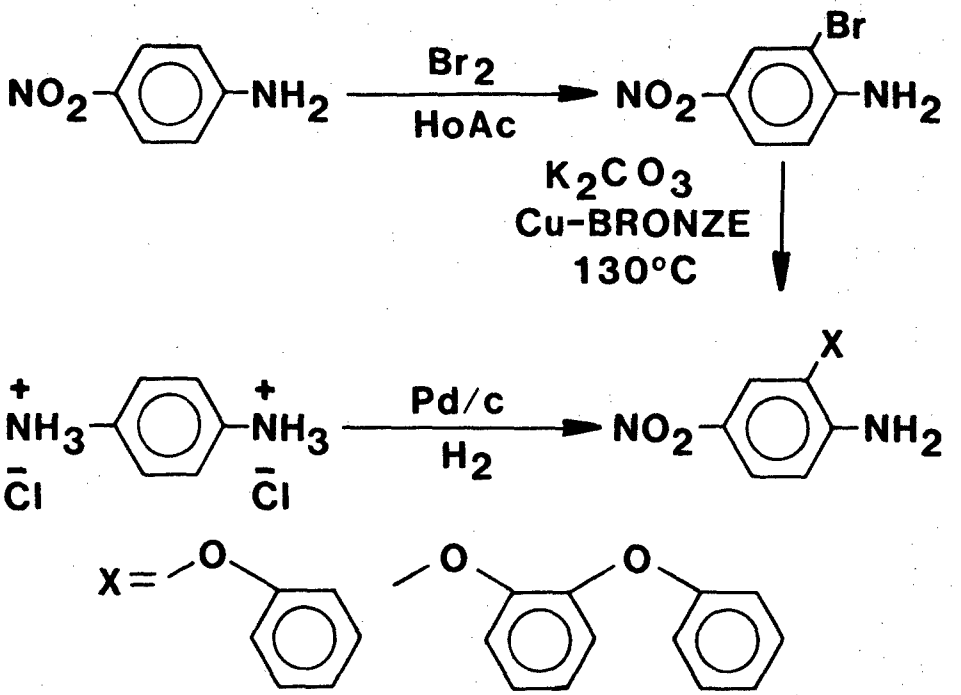


Figure 8. Synthetic Route to 2-Substituted p-Diaminobenzene Monomers

yield a polyisoimide. Generally, this is a one-pot synthesis and the polyamic acid need not be isolated before proceeding to cyclodehydration. After the polyisoimide has been isolated and carefully dried, it may be thermally isomerized to the corresponding polyimide. The entire procedure is outlined in Figure 9.

A procedure similar to that developed by Sroog was used to synthesize the polyamic acids (Reference 9). Three benzidine analog monomers were reacted in this procedure: the tetramethyl, 3,3'-phenoxy, and 3,3'-(3-phenoxypheyleneoxy) derivatives. A small amount of each of the amic acids was withdrawn from the reaction mixture and its inherent viscosity (ηinh) and IR spectra measured. In all cases after stirring the reactant monomers for approximately 2 hours at room temperature, an increase in the reaction mixture viscosity was noted. This increase in viscosity was more pronounced with the tetramethyl polyamic acid system. The mixture was then usually allowed to stir overnight under nitrogen at room temperature. This additional period of stirring seemed to only slightly affect the reaction mixture's viscosity. Heating (~60-80°C) the reaction mixture had no visible effect on viscosity but did cause a slight darkening of the solution's color. These observations seem to indicate that the majority of the polymerization proceeds quickly at room temperature and is essentially complete in

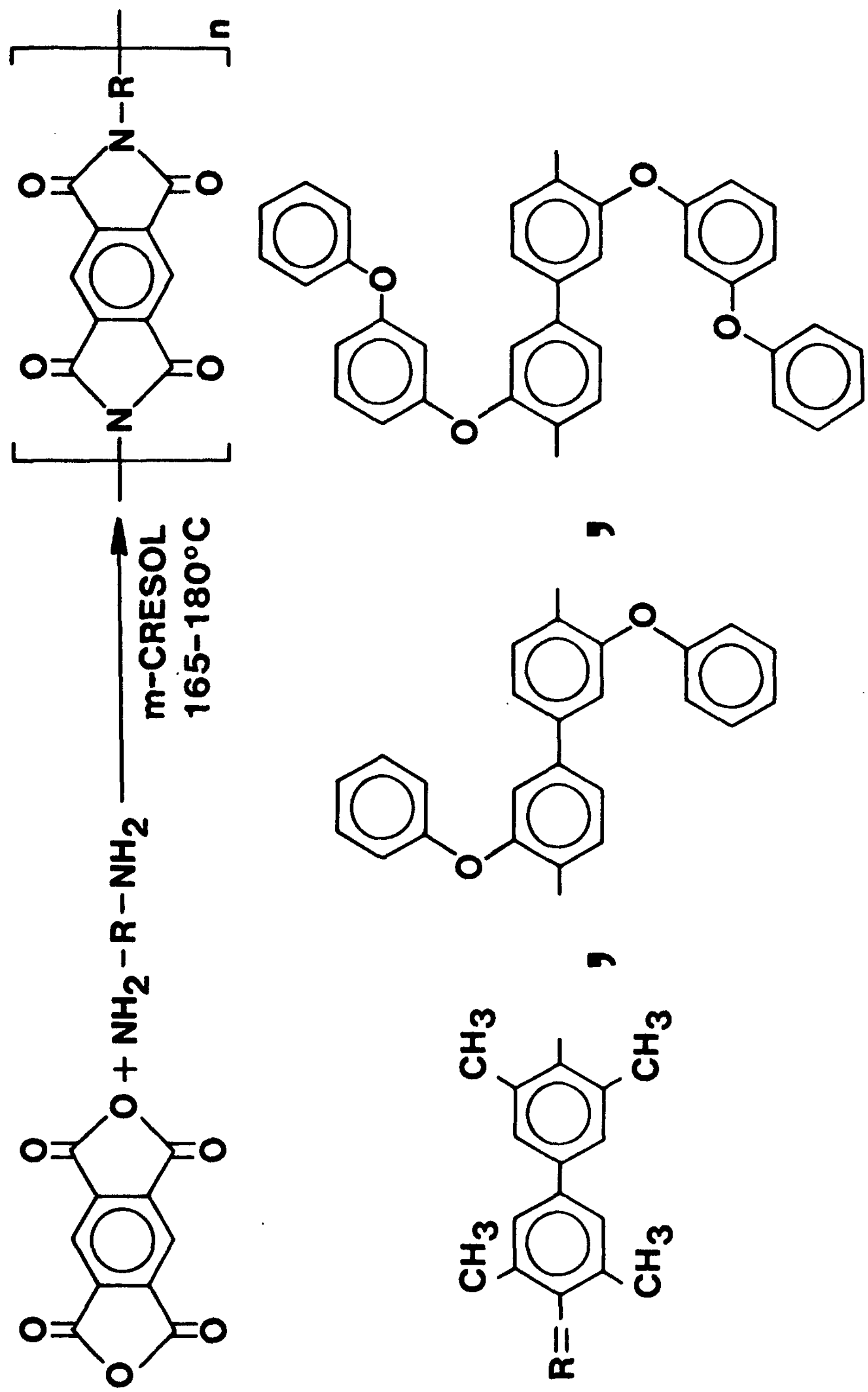


Figure 9. General Route for the Synthesis of Benzidine Derivative Polyisoimides

a few hours. All polyamic acid forming reactions were run with Aldrich Gold Label pyromellitic dianhydride in anhydrous DMAC under dry nitrogen at a 10% weight polymer concentration.

After the formation of the polyamic acid was judged complete, the reaction mixture was diluted with additional DMAC to approximately a 2% by weight polyamic acid concentration. After the dilution with DMAC,a small amount of lithium chloride (LiCl) was added to increase the ionic character of the solution and improve the polyamic acid's solvation. It was later found that the use of LiCl was not necessary in the case of the tetramethyl polyamic acid system. Next a slight excess (2-3%) of DCC was added to the solution (under N_2) to cyclodehydrate the system and to produce the desired polyisoimides. The dehydration agent, DCC, was chosen because it has been previously shown to give high yields of the isoimide and provide an easy way to remove the hydration by-product, in this case dicyclohexylurea (DCU), which is insoluble in most organic solvents (Reference 1). Before the DCC addition, the reaction mixture was usually a very pale yellow color. Upon addition of DCC the solution showed a significant increase in viscosity and a bright orange color developed, which darkened to a deep red after one hour of stirring. The mixture was then stirred for an additional period of time (from 2 to 12 hours) and allowed to stand for approximately 12 hours. During this period a large amount of DCU could be seen to crystallize out of the mixture and fall to the bottom of the reaction vessel. Most of the essentially DCU-free polymer solution (completely clear and dark red in color) was decanted from the reaction vessel and poured into a large volume of anhydrous isopropanol. This procedure results in the precipitation of the polyisoimide as a bright red-orange powder. Isopropanol has been previously shown to be a good precipitating solvent for isoimides in that it solubilizes low molecular weight by-products, such as DCU, and tends to precipitate the polymer as a fine powder rather than a granular mass as occurs when solvents such as hexane are used (Reference 2). Polyisoimides have been known to react with alcohols to form polyamide-esters (Reference 1). Spectral analysis (IR and proton NMR) of the precipitated polyisoimide showed no evidence that this side reaction was occurring. After filtering the polymer from the isopropanol mixture, it was washed with several more portions of isopropanol and dried under vacuum at 40°C until a constant weight was achieved. This dried polyisoimide (very dark red in color) was quite hard and dense in structure and proved to be only slightly soluble in aprotic solvents. This led to the

development of a different workup procedure to increase the polymer surface area and improve solubility. The improved procedure centers around not allowing the fluffy, wet, powdered precipitate to collapse on itself and thus preventing the formation of a hard, dense solid. The precipitated material was collected on a coarse fritted funnel, taking great care to keep the material covered with fresh anhydrous alcohol at all times (essentially never allowing the material to dry out). The precipitate was next washed several more times with fresh isopropanol to remove any remaining DCU and as much as possible of the DMAC solvent, and finally washed with several portions of anhydrous benzene to remove most of the isopropanol wash solvent. The final benzene/polyisoimide slurry was freeze dried for at least 72 hours. Benzene was chosen as the freeze drying solvent because of its appropriate freezing point and vapor pressure. The resulting product was a bright red-orange, light, spongy cake. This procedure (outlined schematically in Figure 10) greatly increased the solubility of both the tetramethyl and 3,3'-(3-phenoxyphenyleneoxy) benzidine derivative polyisoimides. Clear solutions up to 10% by polymer weight were made using DMAC as a solvent. The 3,3'-phenoxybenzidine derivative polyisoimide system did not show a corresponding increase in solubility. Its solubility did increase slightly, but not enough to make solutions of even moderate concentration. After freeze-drying, where possible, the inherent viscosity measurement and IR analysis of the polymer were conducted.

b. Preparation of 1,4-Diaminobenzene Derivative Polyisoimides

The route developed to synthesize these polyisoimides was quite similar to that used in the preparation of the benzidine derivative polymers. The primary difference in the synthesis was the requirement that the 1,4-diaminobenzene monomers (both the 2-phenoxy and 2-(3-phenoxyphenylenoxy derivatives) be introduced into the polyamic acid synthesis step as hydrochloride salts. As previously indicated, the free amine monomers could not be isolated because of their oxidative instability. Initial attempts to polymerize the diamine hydrochloride salts with pyromellitic dianhydride relied on DMAC to deprotonate and generate the free diamine. This procedure produced no observable increase in the reaction mixture's viscosity and only very low molecular weight material was isolated. This may be a result of DMAC not being basic enough to completely deprotonate the diamino salt. Other side reactions may dominate in this case. In order to produce the free diamine at an accelerated rate a stronger base, lithium

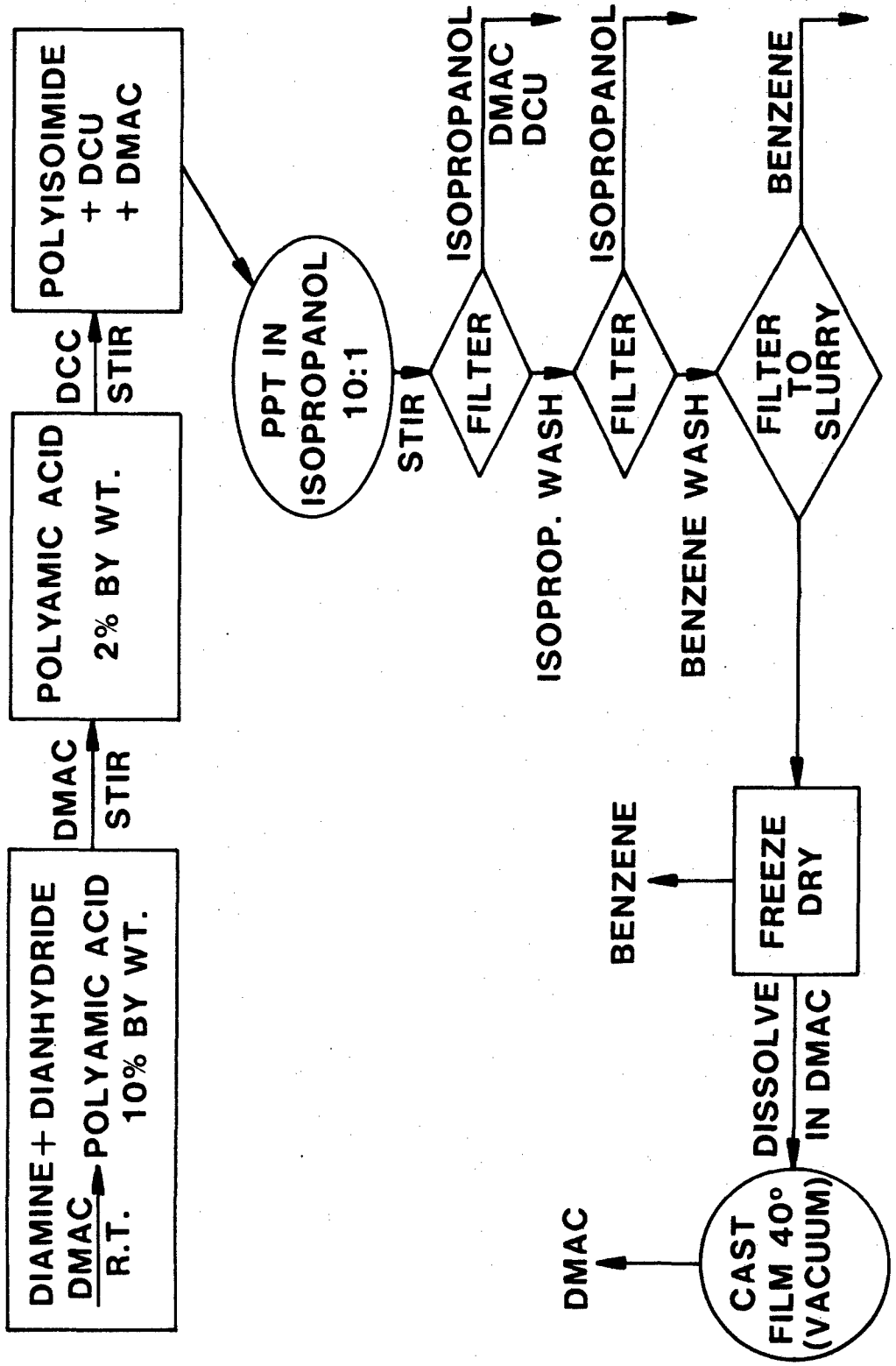


Figure 10. Schematic Outline of Polyisoimide Synthesis and Isolation

carbonate, was employed. After addition of starting monomers, base and stirring with solvent, gas evolution was noted. After stirring for a period of 2 hours, a slight thickening of the reaction mixture was noted (this was not observed in the absence of lithium carbonate). The polyamic acid solutions were then usually stirred overnight under nitrogen at room temperature. After the indicated period of stirring, the mixture was diluted with anhydrous DMAC to a 2% by weight polyamic acid concentration. Next, the appropriate amount of DCC was added to cyclodehydrate the system to the polyisoimide. The bright red-orange product was isolated in the same manner as described for the benzidine derivative polyisoimides. The polymers were found to be soluble in both DMAC and THF, but appeared to be of relatively low molecular weight as compared to the benzidine derivative polyisoimides (based on inherent viscosity measurements). Since these polymers were synthesized on very small scale, the polyamic acid intermediates were not isolated.

c. Preparation of Benzidine Derivative Polyimides

For structural characterization it was necessary to synthesize directly at least some polyimide polymers with structures identical to polyimides produced by thermal isomerization of the polyisoimides of interest. Polyimides were produced for each of the corresponding benzidine derivative polyisoimides (tetramethyl, 3,3'-phenoxy, and 3,3'-(3-phenoxy-pheyleneoxy) derivatives). A procedure developed by Harris et al. (Reference 10) was used to produce the required polymers and is outlined in Figure 11. In all cases, the polyimides precipitated before any appreciable molecular weight was achieved. The beige solids were collected by filtration and washed several times with methanol and dried at 150°C under vacuum for 48 hours. The polyimides proved to be insoluble in both aprotic and common organic solvents (including DMAC and THF). The IR spectra of all three polyimides were recorded. Polyimides of the corresponding 1,4-diaminobenzene derivative polyisoimides were not synthesized.

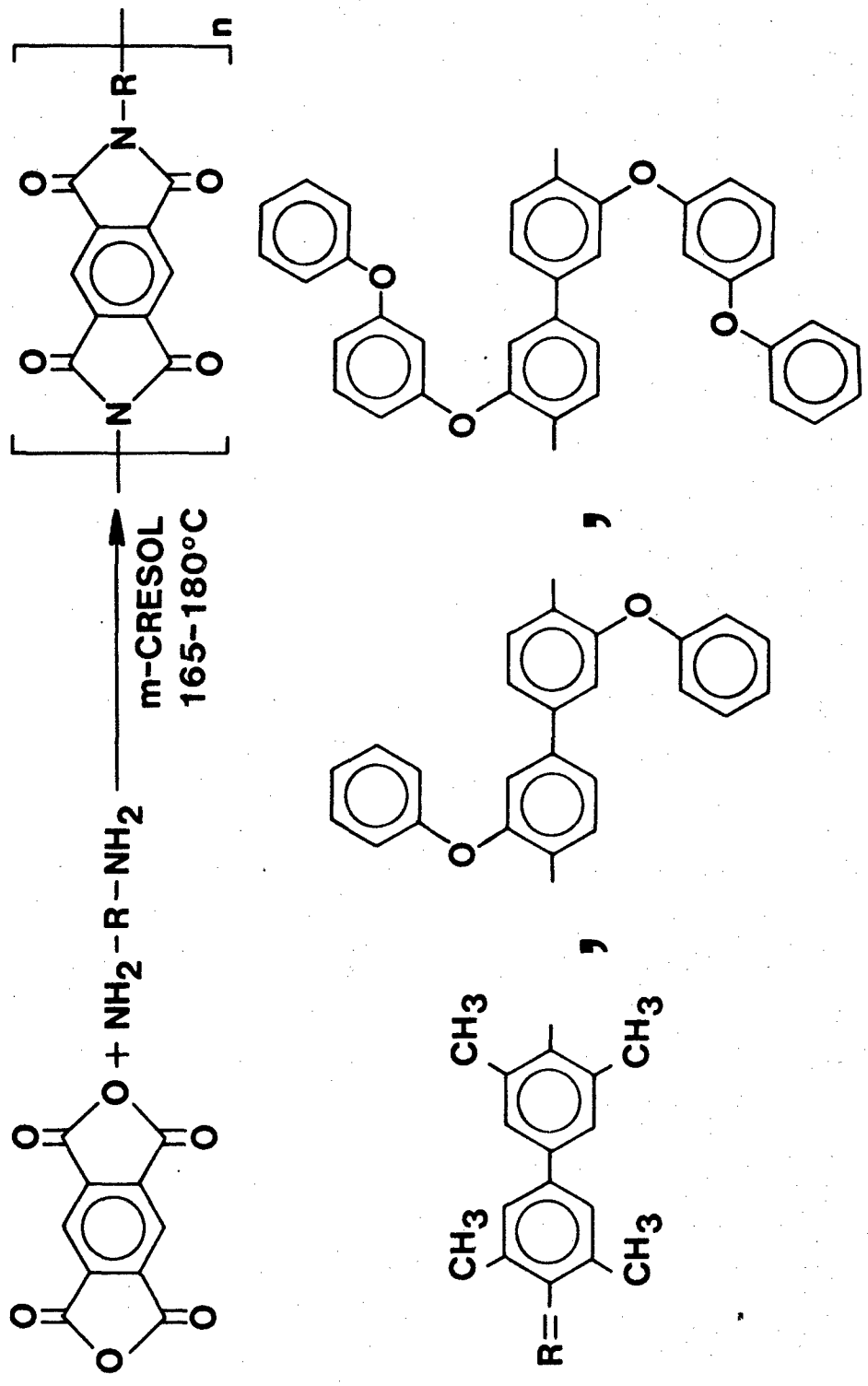


Figure 11. General Route for the Direct Synthesis of Polyimides

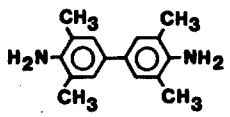
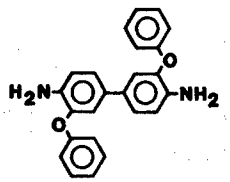
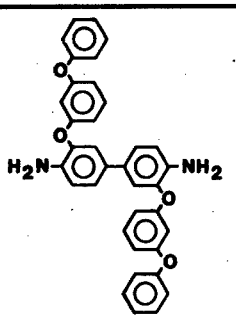
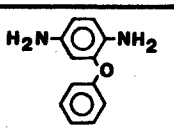
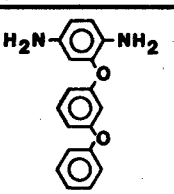
4. POLYMER CHARACTERIZATION

a. Inherent Viscosity (I.V.) Measurements

In an effort to determine relative molecular weights of the newly synthesized polymers, inherent viscosity measurements were made. All measurements were made in DMAC. Polyamic acid I.V.'s for all benzidine derivative systems were measured. As previously stated, the polyamic acids of the 1,4-diaminobenzene derivatives were not isolated and no I.V. measurements were obtained for these systems. An attempt was made to measure I.V.'s of all the synthesized polyisoimides. The 3,3'-phenoxybenzidine derivative was only slightly soluble in DMAC and only very dilute solutions could be formed. As a result it was decided not to report any I.V. value for this polyisoimide system. The insolubility of the polyimides synthesized precluded the possibility of measuring their I.V.'s. All collected I.V. data are summarized in Table 1. The reactions used to prepare the polyamic acids (as well as the polyisoimides) were repeated several times and I.V.'s of the products measured each time. Only the highest values achieved have been reported. The tetramethyl system consistently showed the highest I.V. and the 3,3'-(3-phenoxy-phenyleneoxy) system, the lowest. Two factors can be proposed to account for this trend. First, the commercial availability of the tetramethyl benzidine may have provided a monomer with higher and more consistent purity than that of the diamine monomers produced in house. Second, it can be observed that the size of pendent groups increases the I.V.'s of the polyamic acids decrease. This points to possible steric hindrance effects influencing the rate of polymerization. Also, some problems were encountered in the catalytic reduction of 3,3'-(3-phenoxyphenyleneoxy)-4,4'-dinitro biphenyl to the 3,3'-(3-phenoxyphenyleneoxy)benzidine monomer. Large amounts of catalyst (10% palladium on charcoal) had to be used and yields were lower than for the reduction of the 3,3'-phenoxy derivative. This, again, may be associated with the presence of a large substituent ortho to the reactive group (in this case nitro). As expected, a corresponding trend was observed for the polyisoimide I.V.'s. The tetramethyl system had by far (by a factor of 2) the highest I.V. of this group. The polyisoimides of the 1,4-diaminobenzene derivatives showed significantly lower I.V.'s than the benzidine derivative polyisoimides. This is probably due to the fact that the hydrochloride salts of the 1,4-diaminobenzene monomers were used in the polymerizations, rather than free amines. As is usually the case with amino

TABLE 1

INHERENT VISCOSITY VALUES FOR POLYMERS

POLYMER / AMINE	INHERENT VISCOSITY VALUE FOR POLYMERS		
	POLYAMIC ACID	POLYISOIMIDE	POLYIMIDE
	1.11 (DMAC)	1.89 (DMAC)	INSOLUBLE
	0.97 (DMAC)	VERY SLIGHTLY SOLUBLE (DMAC) +LiCl	INSOLUBLE
	0.85 (DMAC)	0.93 (DMAC) + LiCl	INSOLUBLE
	NOT ISOLATED	0.33 (DMAC)	NOT SYNTHESIZED
	NOT ISOLATED	0.25 (DMAC)	NOT SYNTHESIZED

salts, there is some indication from elemental analysis that hydrates of the salts were present. This would affect the overall stoichiometry of the polymer reaction. Efforts were made to quantify the amount of water present from elemental analysis but the results were inconclusive. Attempts to break suspected hydrates by drying at elevated temperatures (>80°C) under high vacuum over phosphorus pentoxide only resulted in decomposing the diamines (loss of HCl probably occurred). As previously observed, the 1,4-diaminobenzene derivative with the larger pendent group had the lower I.V.

b. FTIR Thermal Isomerization Study

The isomerization of the new polyisoimides to polyimides was investigated by an infrared (IR) spectroscopy study. It was of particular interest to see if the reaction would occur in the solid state and, if so, at what temperature. Only the tetramethyl benzidine derivative system was evaluated in detail. It was chosen because it had previously been scaled up to evaluate its processing characteristics, and was available in sufficient quantity for the isomerization study. All the spectra referred to in the following discussion are associated with this system.

Interpretation of IR spectra in this study are based, in part, on comparison with the spectra of N-phenyl phthalisoimide and N-phenyl-phthalimide (Reference 11). Other general references were also consulted (References 12 through 15).

Initially the IR spectra of transparent films of freshly prepared polyamic acid and polyisoimide were recorded at room temperature by FTIR. Bands of importance in the polyamic acid spectrum (Figure 12) are acid hydroxy group (broad strong band 2400 - 3500 cm^{-1}), amide nitrogen-hydrogen stretch (medium single band 3230 cm^{-1}), methyl carbon-hydrogen stretch (medium single band 2960 cm^{-1}), acid carbonyl attached to phenyl ring (strong single band 1720 cm^{-1}), amide carbonyl attached to phenyl ring (strong single band 1640 cm^{-1}), amide nitrogen-hydrogen bond (strong single band 1540 cm^{-1}), and carbonyl carbon-oxygen stretch (strong double band 1320 - 1270 cm^{-1}). Significant bands in the polyisoimide spectrum (Figure 13) are isoimide carbonyl (strong single band 1810 cm^{-1}), imine group (strong double band 1640 - 1760 cm^{-1}), and lactone ring with exocyclic double bond (strong single band 920 cm^{-1}). After the room temperature measurements were

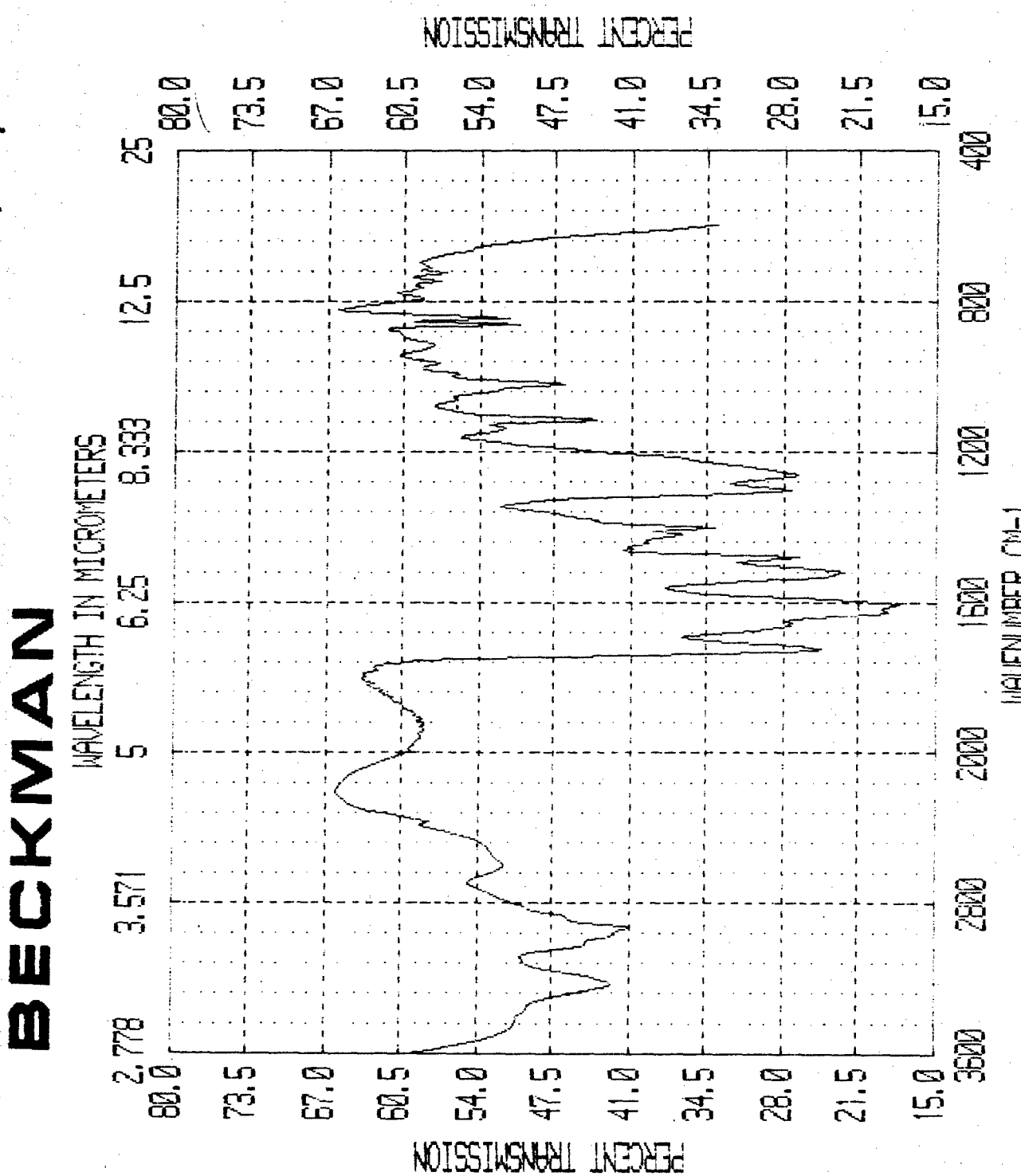


Figure 12. Infrared Spectrum of the Tetramethylbenzidine Based Polyamic Acid

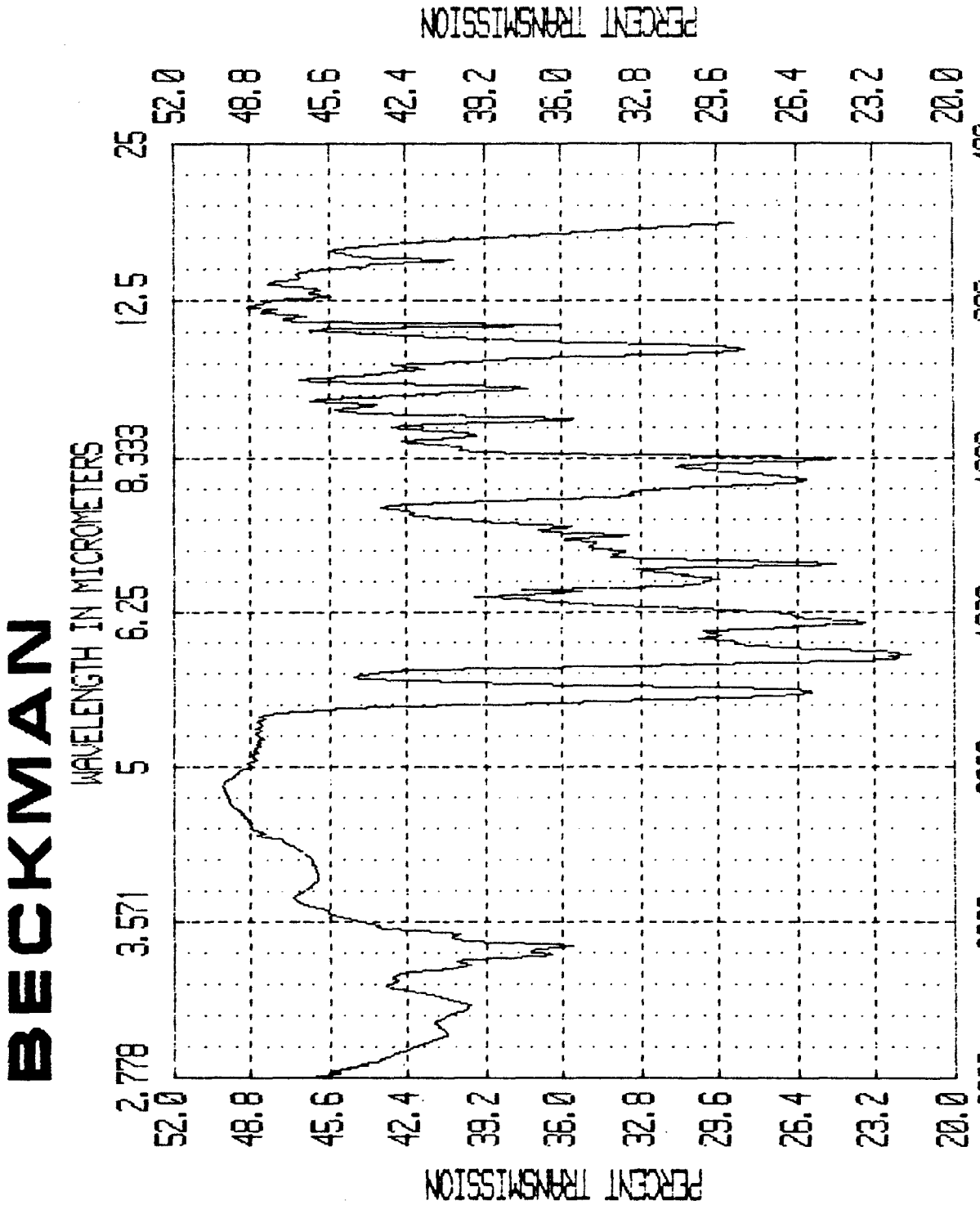


Figure 13. Infrared Spectrum of the Tetramethylbenzidine Based Polyisoimide

complete, a freshly prepared polyisoimide film was placed in a heatable cell. Next a baseline room temperature spectrum (Figure 14) on a convenient scale was run and a heating program initiated. During heating, spectra were run approximately every 10 minutes to follow any developing changes. After heating at 100°C for 1 hour, the spectrum shown in Figure 15 was recorded. Examination of the spectrum shows the carbonyl band (1810 cm^{-1}) and the lactone ring with exocyclic double bond band (920 cm^{-1}) are greatly reduced in intensity. Other small changes in the spectrum are also evident, but interpretation of these differences has not been attempted (the band at approximately 2300 cm^{-1} is from atmospheric carbon dioxide). After heating for an additional 2 hours at 215°C, the spectrum shown in Figure 16 was recorded. The spectrum shows the bands which are characteristic of an imide. Significant bands in the spectrum are imide carbonyl bands (single weak band at 1790 cm^{-1} is carbonyl asymmetric stretching and the single strong band at 1720 cm^{-1} is carbonyl symmetric stretching) and the imide ring band (medium band at 1380 cm^{-1}). A comparison of the IR spectrum of the thermally isomerized polyisoimide with a spectrum of the directly prepared tetramethyl benzidine polyimide (Figure 17) provides a measure of confidence in assigning an imide structure to the former system. The spectra are quite similar with band positions which match one for one in the majority of cases. Some of the bands do differ in intensity and shape, but this may be related more to molecular weight and purity differences than basic structure. The spectra provide good evidence that the isomerization reaction to the imide is quite complete with very little isoimide or polyamic acid remaining. The polyisoimide spectrum indicates there is very little, if any, DCU left in the sample film after processing (based on a comparison with an authentic DCU IR spectrum). Probably the hardest thing to quantify is the amount of polyamic acid present in the polyisoimide samples. Comparison of the polyamic acid and polyisoimide spectra seems to indicate a very low ratio (if any) of amic acid to isomimde, but only an estimate is possible. Finally, there is IR spectral evidence that both the polyamic acid and polyisoimide slowly hydrolyze to their respective acids at room temperature even at low humidity levels. This suggests that the system may be quite sensitive to any water present during the polymer workup procedure and should be handled in an anhydrous manner.

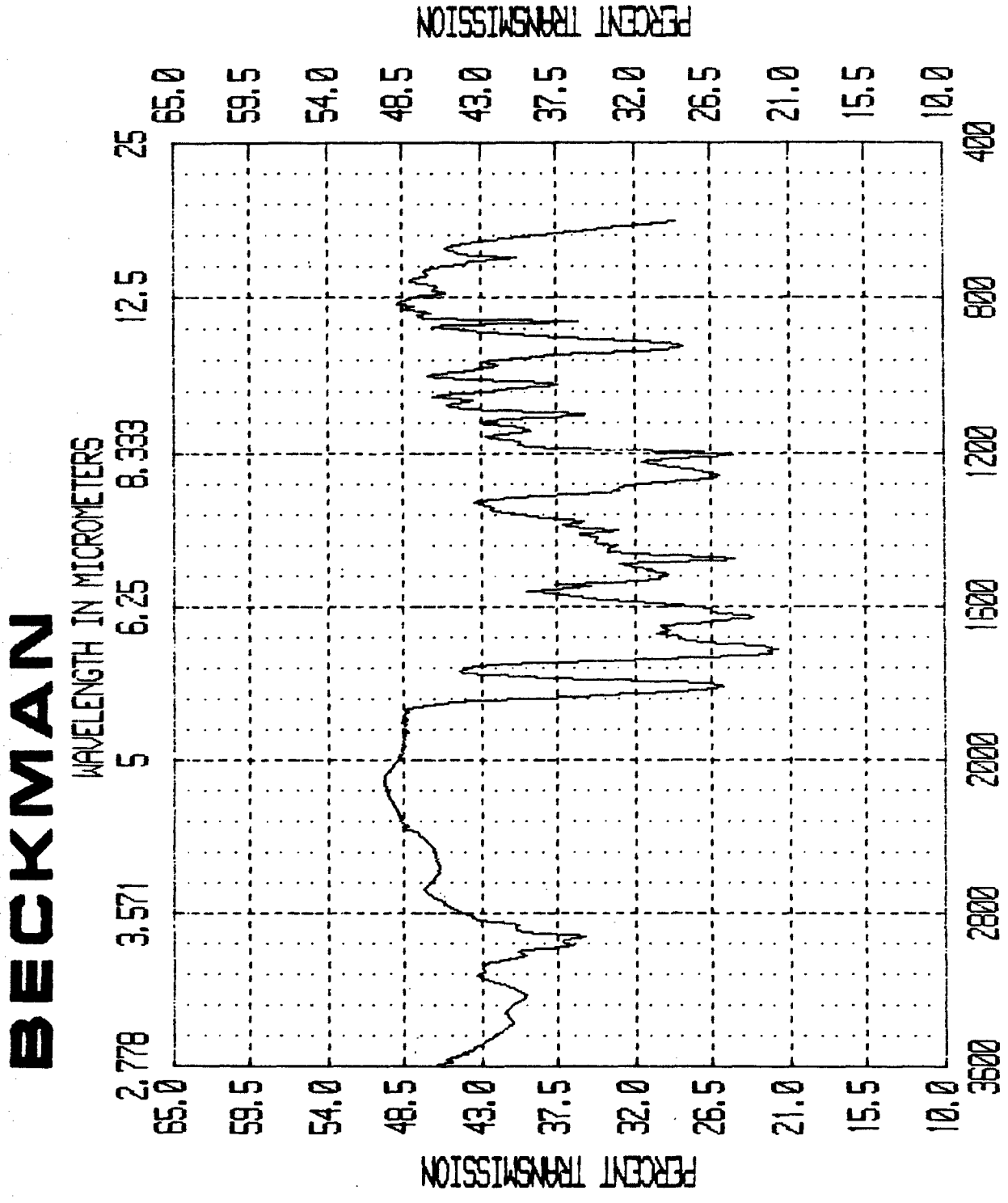


Figure 14. Infrared Spectrum of the Tetramethylbenzidine Based Polyisoimide at Start of Heating Cycle

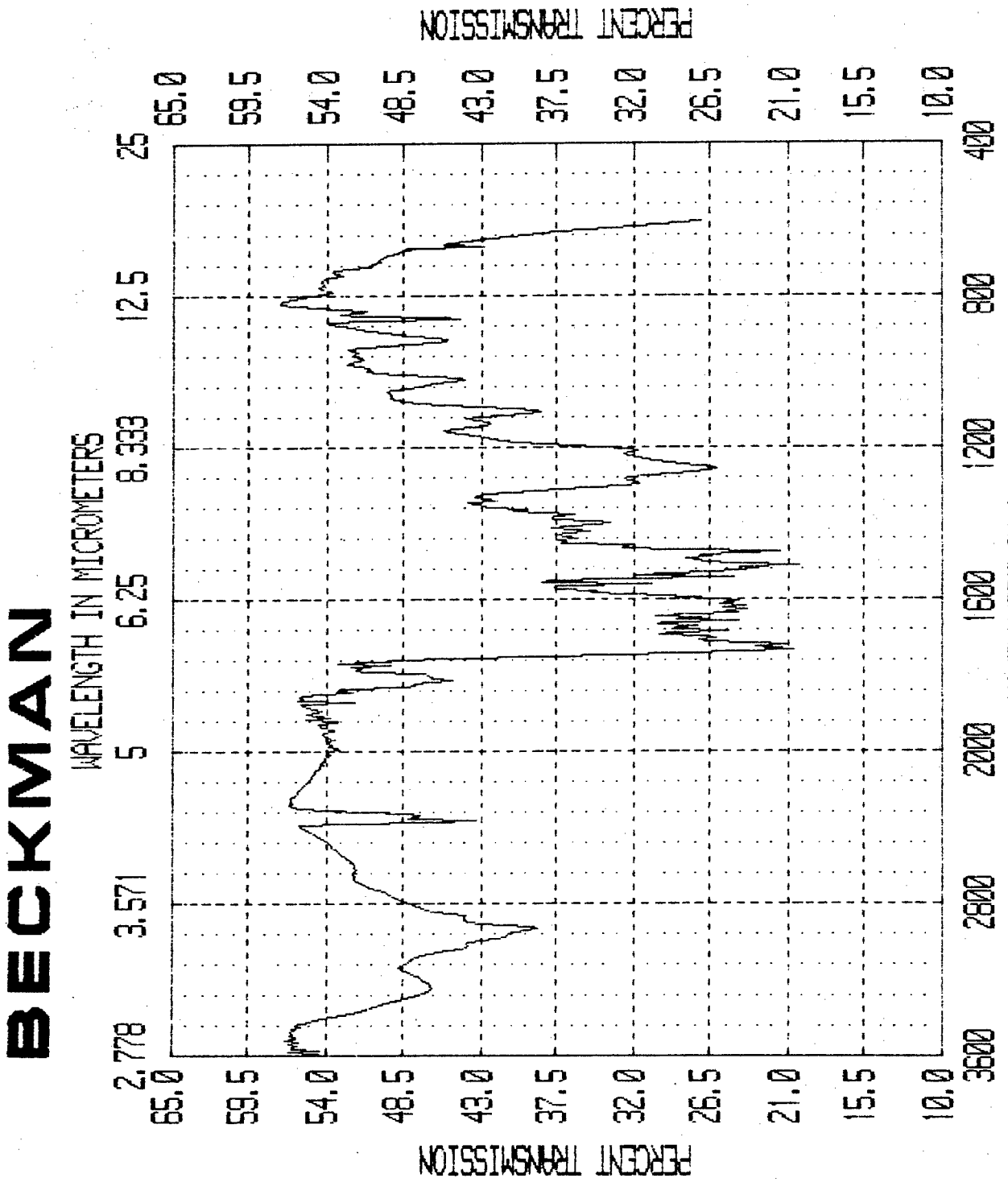


Figure 15. Infrared Spectrum of the Tetramethylbenzidine Based Polyisoimide After Heating at 100°C for 1 Hour

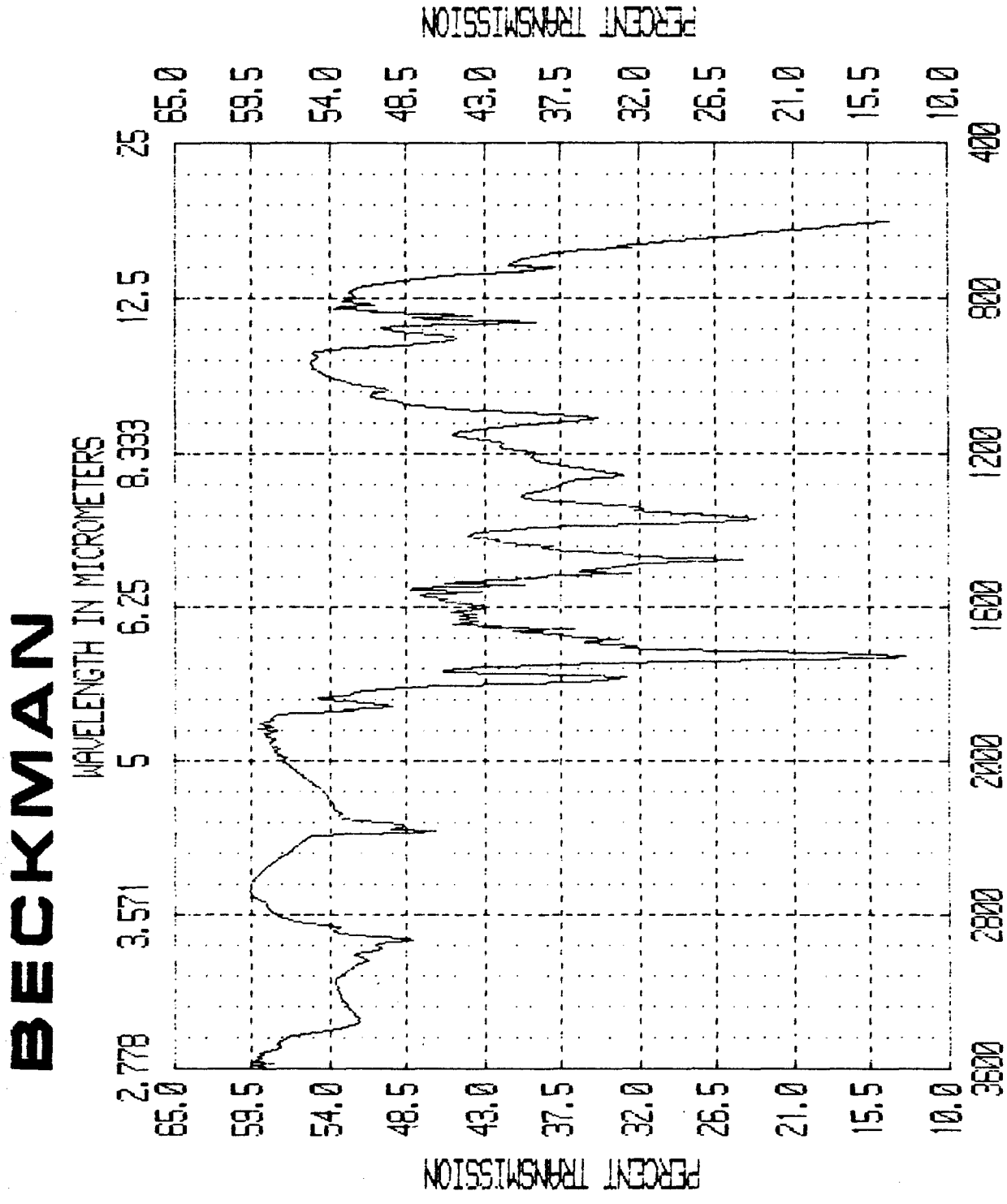


Figure 16. Infrared Spectrum of the Tetramethylbenzidine Based Polyisoimide After Heating for an Additional 2 Hours at 215°C

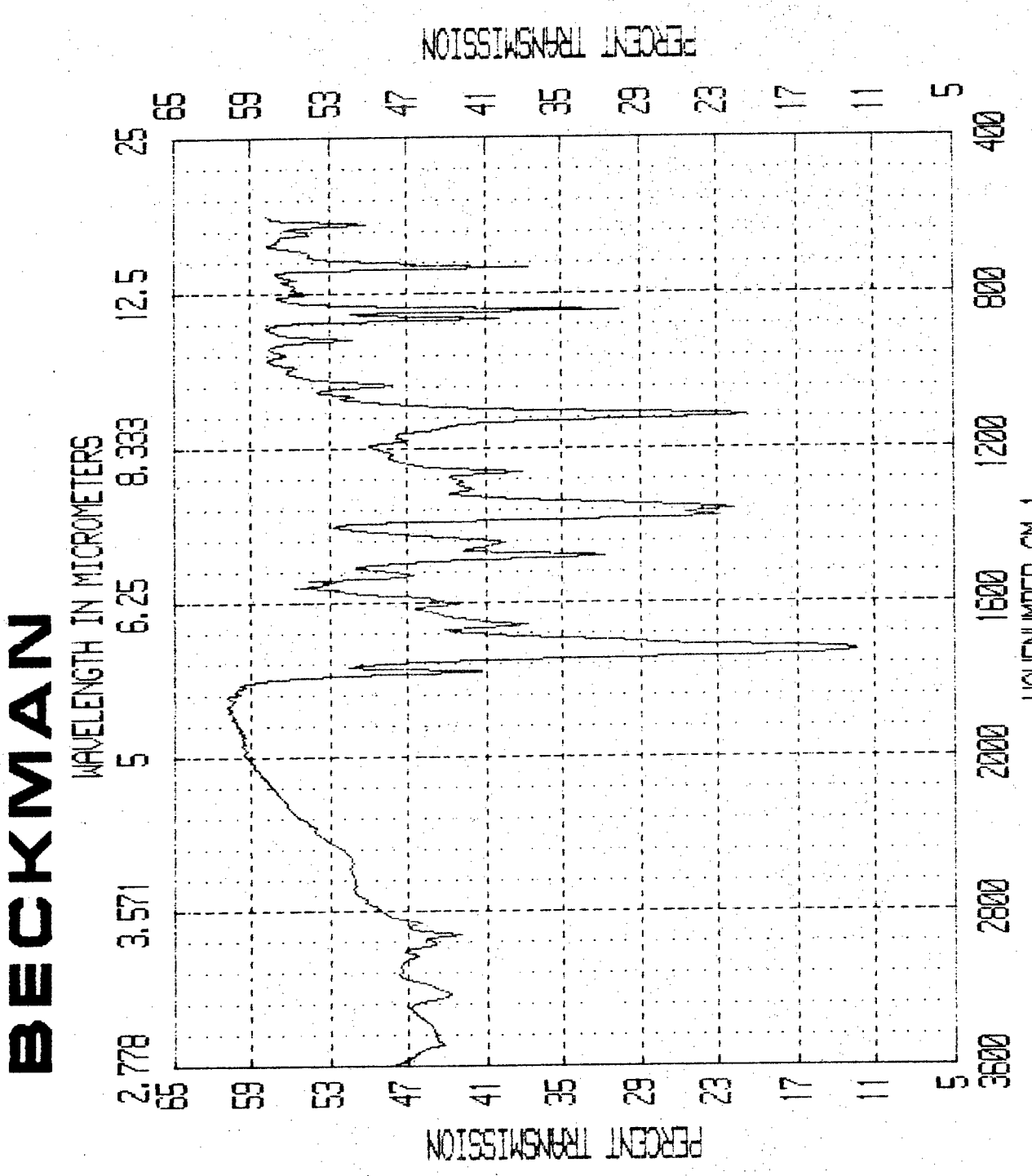


Figure 17. Infrared Spectrum of the Tetramethylbenzidine Based Polyimide

5. POLYMER PROCESSING EXPERIMENTS

Further polymer properties characterization was investigated by attempting to cast both neat and composite films of the newly synthesized tetramethyl benzidine derivative polyisoimide system. As previously noted, only this polyisoimide was synthesized in sufficient quantity for complete evaluation. In addition to casting neat films for physical properties evaluation, neat transparent films were required for the FTIR thermal isomerization study.

The primary problem associated with producing the required strong, thin, transparent films was removal of the DMAC casting solvent. This was difficult because of its low vapor pressure, high boiling point, and hydrogen bonding properties. The need to remove the solvent quickly at a relatively low temperature (temperatures above ~80°C could cause premature isomerization of the polyisoimide to polyimide) compounded the problem. Casting the films quickly with freshly freeze-dried material was considered important because of the metastable nature of the polyisoimide system.

A technique involving moderate heating (~55°C) and high vacuum (0.1 mm Hg) combined with a standard rotary evaporator proved to be the most practical. Neat films were cast by forming DMAC solutions of the 5 to 40% polyisoimide by weight. The polymer solution was transferred to a wide-mouthed resin kettle, which was placed on a rotary evaporator with a ground glass joint adapter. The rotary evaporator was next rotated at maximum speed, so as to form a thin layer of polymer solution on the walls and bottom of the resin kettle, and with low heating and vacuum (~10 mm Hg) applied. After approximately 30 min. the pressure was decreased further (~0.1 mm Hg) and maintained for at least an additional 2 hours. After completing this cycle, a thin, transparent, bright red-orange film could be easily separated (usually in one piece) from the glass walls of the resin kettle. Films produced in this manner retained the closed shape of the resin kettle. Cutting away the bottom of the film produced a cylinder open at both ends. Cutting along the length of the cylinder gave an open flat piece of film of fairly uniform thickness. Films were stored in the dark under refrigeration after casting.

Composite films were produced in much the same manner as described for the neat films. Three matrix systems were briefly investigated, Raydel ^{R}, Udel ^{R}, and an isoimide thermoset, HR600P. DMAC solutions of the matrix and polyisoimide were prepared and cast as before. Slightly cloudy films, indicating some phase separation, resulted with both the Raydel ^{R} and Udel ^{R} systems. Composite films cast with HR600P, however, were completely clear and showed no signs of phase separation. The similarity of the HR600P structure to the polyisoimide may account for the greater homogeneity of the system. Further evaluation of these films is currently under way.

SECTION IV

CONCLUSIONS

The synthesis of several soluble (in DMAC) polyisoimide systems has been accomplished. The most easily prepared of the new systems is the tetramethyl benzidine based polyisoimide. Not only is the polymer soluble at fairly high concentration (~3-5%), but it also exhibits the highest I.V. of the newly synthesized polymers. The tetramethyl benzidine based system was scaled to the 10-g level and both neat and composite films cast from DMAC. Films cast with HR600P resin and the new isoimide system showed no phase separation even after extended periods of thermal treatment. A brief study of the thermal isomerization of the polyisoimide to the polyimide was conducted by FTIR.

Further study is required to more fully characterize the tetramethyl benzidine based system. A good understanding of this system might allow it to serve as a general model for the development of new molecular composite systems. The thermal isomerization should be studied with both proton and carbon 13 NMR. These investigations could be carried out in the solution phase (using deuterated DMAC) with a heatable probe. Additional information on the system's molecular weight is also important for a better understanding of polymer properties. Finally, a complete thermomechanical and physical properties evaluation should be completed, including polymer processing experiments. A more thorough investigation of the synthetic work up of the tetramethyl benzidine based system should focus on the determination of impurities present in the final product (including amic acid and imide present) and the development of anhydrous work-up procedures to present any system hydrolysis. Determination of the polyisoimide's useful shelf-life and its optimum storage conditions would provide more uniform control over the material's quality.

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